

STUDIES IN KINETICS AND MECHANISM OF LIGAND EXCHANGE REACTIONS OF SOME Ni (II) COMPLEXES

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By
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to the

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
JULY, 1979

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STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, under the supervision of Professor P.C. Nigam.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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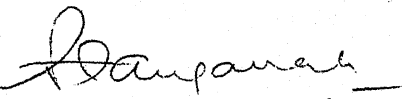
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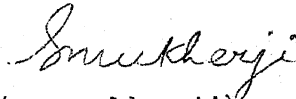
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This is to certify that Mr. Krishan Kumar has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

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Chm 542 Advanced Inorganic Chemistry II
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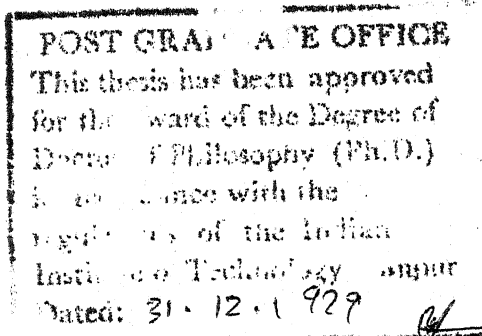

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CERTIFICATE II

Certified that the work contained in this thesis titled, "STUDIES IN KINETICS AND MECHANISM OF LIGAND EXCHANGE REACTIONS OF NICKEL(II) COMPLEXES" has been carried out by Mr. Krishan Kumar under my supervision and the same has not been submitted elsewhere for a degree.

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Kanpur,
July 1979



ACKNOWLEDGEMENTS

I wish to express my feelings of sincere gratitude to Professor P.C. Nigam for suggesting the research problem and providing guidance and inspiration throughout the period of my stay in the research programme. He has been kind and affectionate to me and has encouraged me during periods of experimental difficulties and emotional disturbances.

I am also grateful to Professors U.C. Agarwala, P.R. Singh, S.S. Katiyar and P. Gupta-Bhaya for their kind interest and encouragement.

I wish to acknowledge the valuable comments obtained from Professor James D. Carr, Department of Chemistry, University of Nebraska, Lincoln (U.S.A.) on a portion of work embodied in this thesis. I am also indebted to Professor D. Banerjea, Sir Rash Behari Ghosh Professor of Chemistry, University of Calcutta (India) for giving some valuable suggestions when he visited the department in 1978.

I am thankful to my coworkers Mrs. M. Phull and Mr. H.C. Bajaj for their help in the preparation of thesis and friendly discussions. It is my pleasure to thank some of my friends Messrs Vinod, Anil Chaudhry, I.A.K. Reddy, S. Dinesh Kumar, Raaj Kumar, R.M. Hallen and others for helping me in various matters at different times.

I thank to Messrs R.K. Sharma, T.G. Rao and R.K. Jha for technical assistance, Mr. M.D. Pandey and Mr. L.P. Tripathi for procuring chemicals, Mr. R.K. Bajpai for preparing drawings and Mr. J.N. Sharma for making glass apparatus. The help provided by Mr. K.K. Bajpai and Mr. Anil Kumar is thankfully acknowledged.

I thank Mr. R.D. Singh for typing this thesis with meticulous care and neatness.

I also thank the I.I.T. Kanpur, the C.S.I.R., and the D.S.T. for the financial assistance provided for these investigations.

I am highly thankful to my parents and my brother for helping me to pursue my studies upto the graduate level. I am very much grateful to Mrs. Madhuri Nigam for her kind hospitality and affection. Lastly, I want to thank my wife, Mrs. Pushpa Singh for her patience and understanding during the course of this research programme, and my daughter Shalini who provided entertainment to us during difficult moments by her innocent talks and actions.

Krishan Kumar

PREFACE

The study of reactions involving displacement of polydentate ligands chelated to transition metal ions, say Ni(II), by another uni- or multidentate ligand has attracted the attention of only a few investigators. These reactions pose the difficult problem of interpreting the experimental results in terms of reactivities of the chelates, the stability constants of the reactants and the products, the presence of hydrogen or hydroxyl ions and some other factors. Some data is available on the exchange of aminocarboxylates and to a lesser extent of polyamines by a unidentate ligand viz., CN^- . In either case the information available is limited and some questions such as pH dependence and activation parameters have not been treated adequately.

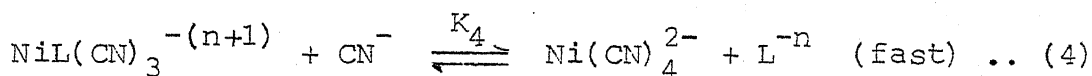
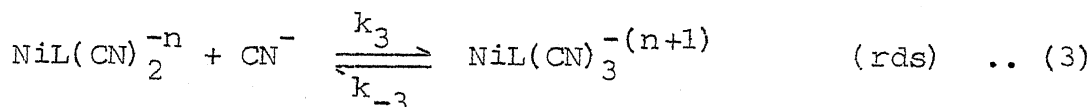
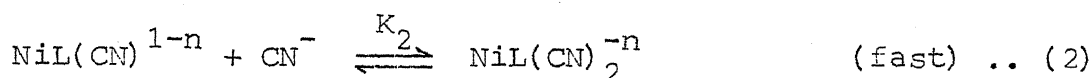
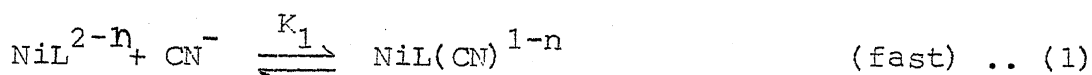
This work was started with the object of understanding the ligand exchange processes in general and polydentate displacement on Ni(II) in particular. Accordingly, this thesis deals with studies involving the kinetics and mechanism of ligand exchange reactions of some mono- and binuclear complexes of Ni(II) with aminocarboxylates and polyamines. The exchanging ligands are either cyanide ions or some aminocarboxylates.

The first chapter of thesis contains a brief survey of the previous work done in this area and emphasizes the scope and importance of the present work. To a good measure the present work has enriched the understanding of intimate mechanistic

details of ligand exchange reactions of Ni(II) complexes. The reactions follow the associative path rather than the dissociative one, that is the formation of a metal ligand bond with an incoming ligand is accompanied by a weakening of a metal ligand bond of the leaving ligand.

The second chapter deals with the experimental data, analysis and interpretation of the results of reactions between a monodentate ligand cyanide and monoaminocarboxylato nickel(II) complexes to produce tetracyanonickelate(II). The aminocarboxylates chosen for the reactions were TMDTA (trimethylenediamine-tetraacetic acid), 1,2-PDTA (1,2-diaminopropane-tetraacetic acid), DTPA (diethylenetriamine-pentaacetic acid) and TTHA (triethylene-tetraamine-hexaacetic acid). The $\text{Ni}(\text{TTHA})^{4-}$ reaction with CN^- has been studied earlier by one research group but the results and interpretations presented here are at variance with them. The reaction conditions for all these reactions were $\text{pH} = 11.0 \pm 0.2$, $\mu = 0.1 \text{ M}$, $\text{temp} = 25 \pm 0.1^\circ\text{C}$. The forward reactions were carried out in presence of large excess of CN^- . The rate data showed first order dependence in NiL (L = an aminocarboxylate ligand) and a variable order dependence in cyanide. There was kinetic and spectrophotometric evidence for the formation of mixed ligand complexes of the type $\text{NiL}(\text{CN})_x^{2-n-x}$, where x may be 0, 1 or 2. In these four cases the order in cyanide was two and one. The reverse reactions were forced in presence of large excess of ligands over $\text{Ni}(\text{CN})_4^{2-}$. The reactions were first order each in $\text{Ni}(\text{CN})_4^{2-}$ and L^{n-} and inverse first order in cyanide.

There was also kinetic evidence for the formation of mixed ligand complexes of the type $[\text{NiL}(\text{CN})_3^{-(n+1)}]$ in each case. The results lead to a four step mechanistic scheme given below:

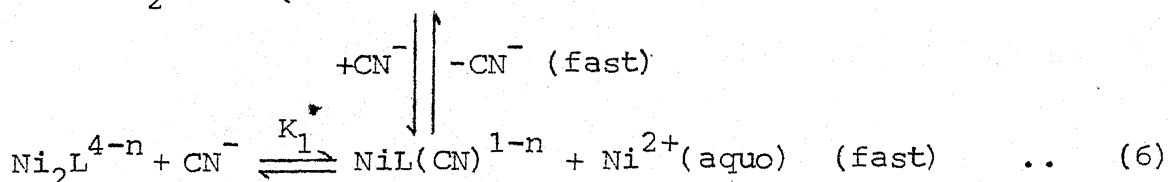
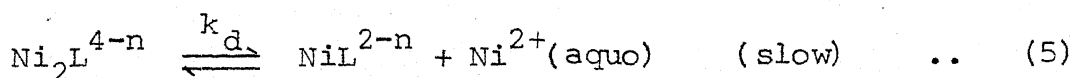


The transition between NiL^{2-n} and $\text{Ni}(\text{CN})_4^{2-}$ is kinetically controlled by the presence of three cyanides around nickel ion in the rate determining step. The activation parameters and the stability constants of intermediates produced in these steps nicely support this mechanism.

The pH dependence of the forward rate makes it possible to resolve the rate constants due to CN^- and HCN which is also a reactant below pH 9, whereas the pH dependence of the reverse reaction to interpret the results in terms of the reactivities of protonated forms of the ligand HL^{-n+1} , $\text{H}_2\text{L}^{-n+2}$ etc. The dependence of reverse rate on the concentration of sodium ion added as NaClO_4 for ionic strength control provides a kinetic method for evaluating the stability constants of the weak NaL^{-n+1} complexes. The method may be extended for estimating the stability constants of other alkali metal complexes of

aminocarboxylates. A correlation between rate constants and overall stability constants of intermediates has been attempted.

Chapter three deals with the reaction behaviour of two binuclear complexes of nickel viz., $\text{Ni}_2(\text{TTHA})^{2-}$ and $\text{Ni}_2(\text{DTPA})^{1-}$ with cyanide ions. Although some work is reported on the ligand exchange reaction of binuclear complexes of Pt(II) and Pd(II) but very little data is available for the reaction of binuclear complexes of Ni(II) . During the course of investigation it was found that the present results differ from those reported by one research group for Ni_2TTHA reaction with cyanide. A plot of $\log (\text{rate constant})$ vs $\log [\text{CN}^-]_{\text{T}}$ showed a zero order dependence in cyanide at low concentration of CN^- in both cases and first order dependence in case of DTPA and second order dependence in case of TTHA at higher concentration level of cyanide. The zero order dependence is interpreted to mean that the $\text{Ni}_2\text{L}^{4-n}$ complexes dissociate to give NiL^{2-n} and $\text{Ni}^{2+}(\text{aq.})$ in a slow step. Another differentiating feature of these reactions is a step involving cyanide assisted dissociation of Ni_2L to give $\text{NiL}(\text{CN})$ and $\text{Ni}^{2+}(\text{aquo})$. These steps are:



The subsequent steps are the same as shown in the mechanism for mononuclear complex reactions with CN^- . The mechanism is supported by additional evidence.

The reactions involving the displacement of another class of multidentate ligands viz., polyamines by cyanide are described in Chapter four. The polyamines chosen were Dien (diethylenetriamine) and Tet (tetraethylene-pentamine). The reaction conditions were : pH range 5.5 - 7.5 $\mu = 0.1$ M and temp = 25°C. At pH values greater than 8.0 these reactions were so fast that they could not be followed by spectrophotometric method. Therefore, higher pH values could not be tried. The mechanism proposed is same as given in Chapter two.

Chapter five deals with the reactions involving displacement of a multidentate ligand Tet from $\text{Ni}(\text{Tet})^{2+}$ complex by other multidentate ligands, viz., HEEDTA (N-(2-hydroxyethyl)-ethylenediamine-N,N',N''-triacetic acid) and TMDTA (trimethylenediamine-tetraacetic acid). The reaction conditions were pH range 5.0-11.5, $\mu = 0.1$ M (NaClO_4) and temp = 25°C. These reactions were followed by the cyanide quenching method taking advantage of the data of Chapter two and four, and rate constants were evaluated by the initial rate procedure. An associative reaction mechanism involving step by step removal of polyamine and simultaneous bond formation by the incoming multidentate ligand has been proposed. The pH dependence of these reactions has been interpreted in terms of reactivities of protonated forms of the complex viz., $\text{Ni}(\text{HTet})^{3+}$, $\text{Ni}(\text{H}_2\text{Tet})^{4+}$.

The last chapter describes the determination of stability constants of complexes of alkali metals with the aminocarboxylates by a kinetic method. These complexes are rather less

stable and the conventional methods are not very useful. In this method the ionic strength is maintained by adding a non-complexing species TMACl (tetramethyl-ammonium chloride) and varying amounts of chosen alkali metal chlorides in place of NaClO_4 normally used in kinetic studies.

The thesis contains figures, tables and appendices, wherever necessary.

Particular care has been taken to give due credit to the work reported by other authors in the literature. The author is fully responsible for purely unintentional oversights and errors which could be traced herein.

ABBREVIATIONS

Asp	-	Aspartic acid
ATP	-	Adenosine triphosphate
BDTA	-	2,3-Diaminobutane-N,N,N',N'-tetraacetic acid
Bipy	-	Bipyridyl
bn	-	Butane diamine
Cal	-	Calmagite
CDTA	-	Cyclohexane diamine tetraacetic acid
dacco	-	1,5-Diazacyclooctane
DGEN	-	Diglycylethylene diamine
Dien	-	Diethylene triamine
N,N'-di-Meen		N,N'-Dimethylethylene diamine
dto	-	Dithiooxalate
DTPA	-	Diethylene triamine pentaacetic acid
EBT	-	Eriochrome Black T
EDMA	-	Ethylenediamine monoacetic acid
EDTA	-	Ethylenediamine tetraacetic acid
EGTA	-	(Ethyleneglycol)bis(2-aminoethyl ether)- N,N,N',N'-Tetraacetic acid
en	-	Ethylenediamine
GEDTA	-	2,2'-Ethylenedioxy bis(ethyliminodiacetic acid)
GGG(TG)	-	Triglycine
glu	-	Glutamic acid
gly	-	Glycine
HEEDTA	-	(Hydroxy ethyl)ethylenediamine triacetic acid

Abbreviations (contd.)

HEIDA	-	(Hydroxy ethyl)iminodiacetic acid
IDA	-	Iminodiacetic acid
MIDA	-	Methyl iminodiacetic acid
mpa	-	2-Methyl-pyridylamine
NTA	-	Nitrilo triacetic acid
PAR	-	4-(2-pyridyl azo) resorcinol
PDTA	-	1,2-Diaminopropane tetraacetic acid
Pent	-	Pentaethylene heptamine
Phen	-	1,10-Phenanthroline
Py	-	Pyridine
Terpy	-	Terpyridyl
Tet	-	Tetraethylene pentaamine
Tet-Meen	-	Tetramethyl ethylene diamine
TMACl	-	Tetramethyl ammonium chloride
TMAOH	-	Tetramethyl ammonium hydroxide
TMDTA	-	Trimethylenediamine tetraacetic acid
Trien	-	Triethylenetetraamine
TTHA	-	Triethylenetetraamine hexaacetic acid

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CHAPTER I

INTRODUCTION

I.1 General: Scope and Object of the Work

Replacement of one ligand coordinated to a metal ion by another is a process which encompasses all aspects of coordination chemistry. It plays an important role in formation, hydrolysis, polymerization and redox reactions. Catalysis and inhibition in metallo-enzyme promoted reactions and transport of metal ions through membranes also have the substitution process as an essential component.

This subject has been documented at some length in recent years.¹⁻⁶ It is about seventy years since the earliest kinetic study of a complex ion reaction was recorded.⁷ It is, however, in the past two decades that a significant drive has been made towards visualising the nature of a variety of intermediates and transition states possible in the reactions of tetra-, penta-, and hexa-coordinated complexes. In such studies many fundamental questions have been only partially answered. It is for this reason that an increasing attention is being paid in recent

years on these aspects of this important and interesting subject.

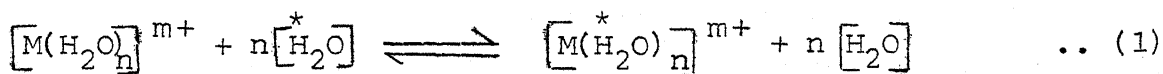
Besides, the reactions of coordination compounds have been investigated to examine various theories of chemical reactivity. Thus the base hydrolysis of pentaamine cobalt(III) ion has been used to study the effect of hydrostatic pressure,⁸ ionic strength⁹ and ion pairing¹⁰ on the reaction rates. Many metal ions are known to act as catalysts in organic and biological systems. Their reactivities may form the basis for better understanding, for example, of striking difference between otherwise similar Ca^{2+} and Mg^{2+} as enzyme activators.¹¹ A case in point is the much faster reaction of Ca^{2+} with ligands such as adenosine-5'-diphosphate, adenosine-5'-triphosphate¹² and a metal ion indicator phthalein.¹³

A knowledge of reaction mechanism can help in devising synthetic routes for new metal complexes and to improve upon the older methods. Basolo,¹⁴ for example, has given a synthetic method for the hitherto unknown nitrito complex ion $[\text{M}(\text{NH}_3)_5\text{ONO}]^{n+}$ where M is Rh(III), Ir(III) and Pt(IV), as a direct sequence to kinetic studies. The successful use of some of the procedures for complexometric estimation of metals depends on difference in rates of complex formation reactions.¹⁵

Although some coordination reactions have been employed to detect¹⁶⁻²⁴ very low concentration of metal ions in solution but sufficient attention has not been paid to rate aspects in

such studies. The use of kinetic methods for estimation of trace elements is now a growing area of research. The catalysis of NiEDTA-Zn²⁺ reaction by Cu²⁺ has been used to estimate Cu²⁺ at 10⁻⁵ M concentration,¹⁹ taking advantage of the fact that the observed reaction rate constant is directly proportional to the catalyst concentration. Similarly Trien²² and Triglycine²³ have been estimated at 10⁻⁵ M concentration level by a kinetic method. It may be emphasized here that a detailed kinetic picture of a reaction is quite often a necessary prerequisite to its use for analytical purposes.

One of the most reliable methods for assigning the solvation number of metal ion involves exchange studies of reactions of the type



Provided the rate of exchange is measurable, and flow methods can help to attain this, the value of n can be determined. In this way the hexa-coordinated structures for $[Al(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ in water^{25, 26} as well as for $[Co(NH_3)_6]^{3+}$ in liquid ammonia²⁷ have been deduced.

Recently the rate data of ligand exchange reactions have been used to calculate the stability constants of mixed metal complexes.²⁸⁻³⁵ The rate data of ligand exchange reactions involving a four step reaction between aminocarboxylato Ni(II) and cyanide ion have been used to calculate the stability

constants³¹⁻³⁵ of mixed ligand intermediates of type $\text{NiL}(\text{CN})_x^{2-n-x}$ (where L = an aminocarboxylate). For such short lived intermediates present in immeasurably small concentrations the conventional methods can not be used.

The study of reactions involving displacement by polydentate ligands chelated to a transition metal ion, say Ni(II), by another uni- or multidentate ligands has attracted the attention of only a few investigators.³⁶ These reactions do not follow the well accepted dictum that "the mechanism of replacement reactions of octahedral complexes, both labile and inert, are dissociative in character and in which bond breaking takes precedence over bond making." These reactions also pose the difficult problem of interpreting the experimental results in terms of reactivities of chelates, the stability constants of reactants and products, the presence of hydrogen or hydroxyl ions and other factors. Some data ^{are} ~~is~~ available on the exchange of aminocarboxylates and to a lesser extent of polyamines complexed to Ni^{2+} by a unidentate ligand viz., the cyanide ion. In either case the information available is limited and some questions such as pH dependence and activation parameters have not been treated adequately.

This work was started with the object of understanding the ligand exchange process in general and polydentate ligand displacement on nickel(II) in particular. Accordingly this thesis deals with studies involving the kinetics and mechanism of ligand exchange reactions of some mono- and binuclear complexes

of Ni(II) with aminocarboxylate and polyamines. The exchanging ligands chosen are either cyanide ion or some aminocarboxylates.

I.2 Classification of Substitution Reactions

The terminology developed by Hughes and Ingold³⁷ for organic reactions has been extended to ligand substitution reactions and two broader classifications viz., nucleophilic substitution and electrophilic substitution for these reactions arise. Another classification, due to Langford and Gray,⁴² anticipates three mechanistic classes of heterolytic substitution reactions in solution viz., dissociative (D), associative (A) and interchange (I) further subdivided into I_a and I_d .

I.3 Literature Survey

The discussions on developments which have taken place in the field of mechanisms of ligand substitution reactions of metal complexes will be mostly restricted to features of the octahedral complexes although the square planar substitution will be alluded to some times.

I.3.1 Replacement of Water Molecules from First Coordination Sphere of Metal Ions in Octahedral Complexes

(A) By unidentate ligands: This is the simplest substitution process one can think of and at least one of the ligands involved will be a solvent molecule. At the moment, reactions of well studied nickel species $Ni(H_2O)_6^{2+}$ ³⁹ will be considered. The second order formation and first order dissociation constants

for replacement of H_2O by a variety of unidentate ligands presenting N, O and F donor atoms according to equation (2) are given in Table I.1 the designation of rate constants given in this table is explained shortly after:

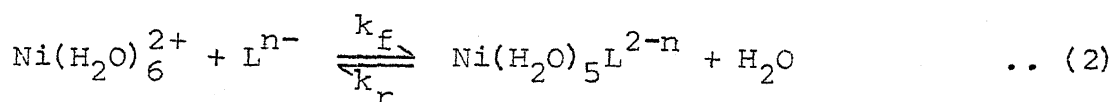


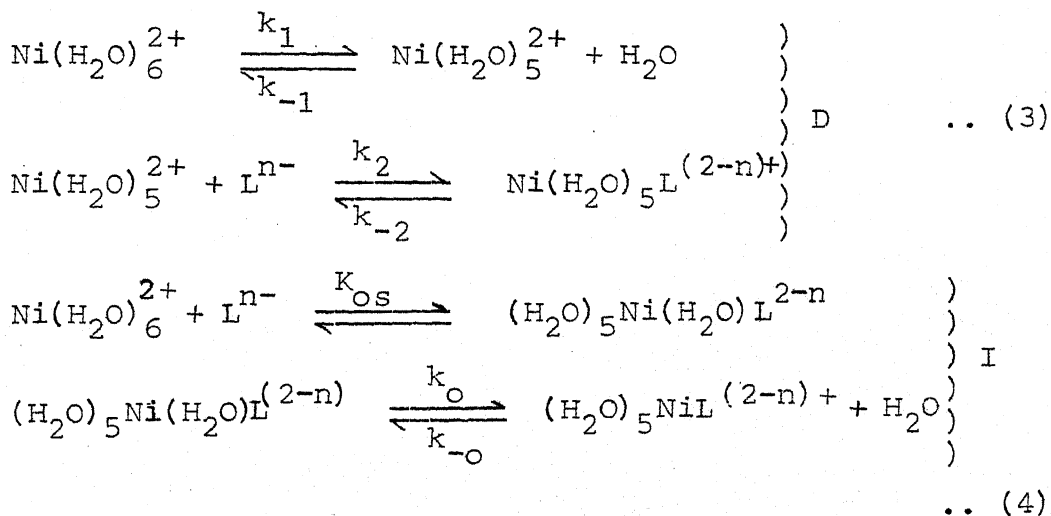
Table I.1. Rate constants⁴⁰ for formation (k_f) and dissociation (k_d) of nickel(II) complexes with unidentate ligands at 25°C.

L^{n-}	$10^{-3} k_f^*$ $\text{M}^{-1}\text{s}^{-1}$	$10^{-3} k_d^\#$ s^{-1}	K_{OS} M^{-1}	$10^{-4} k_o$ s^{-1}	Ref.
SO_4^{2-}	-	100	-	1.5	38
$\text{CH}_3\text{PO}_4^{2-}$	290	7	40	0.7	43
CH_3COO^-	100	5	3	3.0	44
SCN^-	6	0.2	1	0.6	45
F^-	8	2	1	0.8	46
HF	3	-	0.15	2.0	46
H_2O	-	-	-	3.0	47
NH_3	5.0	0.006	0.15	3.0	48, 49
$\text{C}_5\text{H}_5\text{N}$	~ 4.0	0.040	0.15	3.0	49, 50
$\text{C}_3\text{H}_4\text{N}_2$	7.0	0.040	0.15	4.0	51, 52
$\text{NH}_2(\text{CH}_2)_2\text{N}(\text{CH}_3)_3^+$	0.4	0.045	0.02	2.0	49, 51, 53

* $10^{-3} k_f (=K_{\text{OS}} \cdot k_o)$;

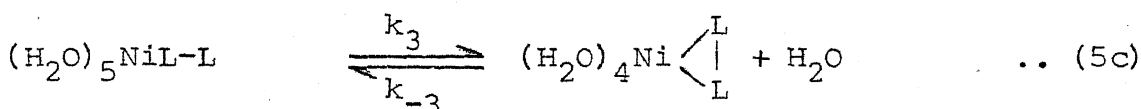
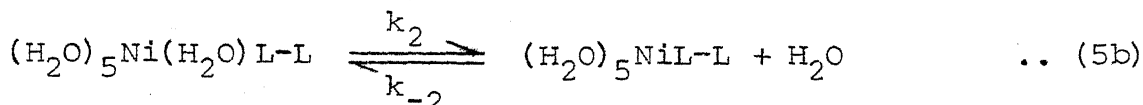
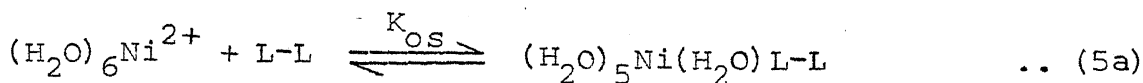
$\#10^{-3} k_d (=k_{-o})$.

The activation energy measured for such type of reactions is reasonably constant. $\Delta H_f^\ddagger = 9-11 \text{ kcal mol}^{-1}$ and ΔS_f^\ddagger values are around zero e.u. This type of data tends to discount an associative mechanism (S_N2) and supports a dissociative one. There have been two main contenders for dissociative mechanisms of octahedral complexes - an S_N1 (lim)⁴¹ or D ⁴² type in which a five coordinated intermediate is generated with sufficient life time to discriminate between different nucleophiles (Eqn. 3) or an S_N1 ⁴¹ or I_d ⁴² type in which the rate determining H_2O-L^{n-} interchange occurs within a very rapidly formed outer sphere complex leading to an inner sphere complex (Eqn. 4). This generally accepted mechanism was originally proposed by Eigen⁵⁴ and elaborated by him and his collaborators:⁵⁴⁻⁵¹



Significantly the value of k_o determined from sound absorption experiments agreed closely with the water exchange rate constants of reaction $\text{Ni(H}_2\text{O)}_6 + \text{H}_2\text{O}^* \rightleftharpoons \text{Ni(H}_2\text{O)}_5(\text{H}_2\text{O})^* + \text{H}_2\text{O}$ determined by NMR broadening experiments.⁴⁷

(B) By bidentate ligands: We can extend the Eigen mechanism⁵⁴ to the formation of monochelate with Equations(5a-5c) representing bidentate ligand by L-L, the inner sphere complex with one end of ligand free by $(\text{H}_2\text{O})_5\text{NiL-L}$ and the final chelated product as NiL_2 (Equation 5c):



Assuming that reaction 5(a) is very rapid compared to 5(b) and 5(c) as well as steady state conditions for the intermediates, Equation (6) is obtained:

$$d[\text{NiL}_2]/dt = k_f [\text{Ni}(\text{H}_2\text{O})_6^{2+}] [\text{L-L}] - k_d [\text{NiL}_2] \quad \dots (6)$$

where $k_f = K_{\text{os}} k_2 k_3 / (k_{-2} + k_3)$

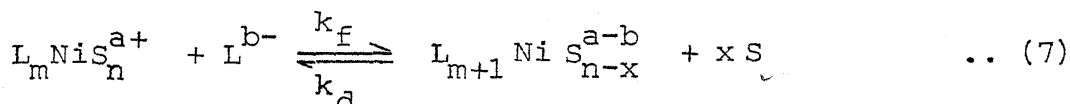
$$k_d = k_{-2} k_{-3} / (k_{-2} + k_3)$$

If $k_3 \gg k_{-2}$ then $k_f = K'_{\text{os}} \cdot k_2$ and $k_d = k_{-2}/K_3$. In this case the overall rate of chelate formation will be determined by the rate of formation of NiL-L species and will be governed by factors applicable to unidentate ligand entry. However, if $k_{-2} \gg k_3$ then $k_f = K_{\text{os}} K_2 k_3$ and $k_d = k_{-3}$ and now the rate determining step (naturally in both direction) will be ring closure (or opening) process. This has been termed sterically controlled substitution

in contrast to normal substitution encountered with first conditions.⁵⁸

I.3.2 Formation Reactions of Multidentate Ligand Complexes

The kinetics of the reaction



(Here S is a solvent molecule)

is among the thoroughly investigated ones in the chemistry of octahedral complexes of Ni(II). The rate law obeyed by these reactions has the general form

$$\text{Rate} = k_f [L_m Ni S_n^{a+}] [L^{b-}] - k_d [L_{m+1} Ni S_{n-x}^{a-b}] \quad \dots (8)$$

so that the pseudo first order rate constant for the forward reaction (complex formation) is

$$k_{\text{obs}} = k_f [L^{b-}] \quad \dots (9)$$

Some values of k_f for the formation of $[NiL(H_2O)_n]^m$ complexes are reported in Table I.2. One interesting observation emerges is that very different entering groups bearing same charge exhibit roughly constant value of k_f .

This behaviour supports a dissociative mechanism in which the entering ligand plays a relatively minor role in the rate determining loss of molecule of solvent. This idea is confirmed by other supporting evidences.⁶⁸ Such reactions involve preliminary diffusion controlled formation of an outer sphere complex

Table I.2. Specific rate constants k_f for the formation of some $[\text{NiL}(\text{H}_2\text{O})_n]^m$ complexes in water at 25°C

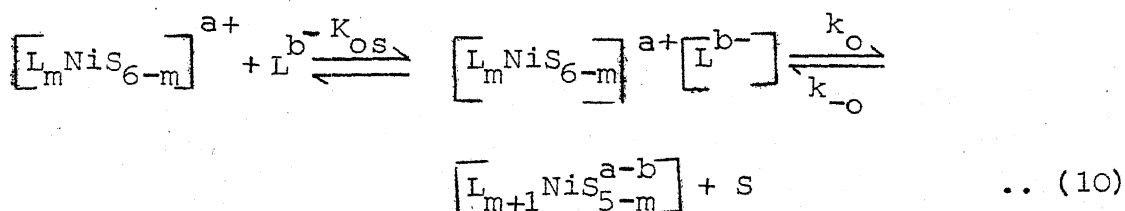
L^{n-}	$10^{-3} k_f, \text{M}^{-1}\text{S}^{-1}$	$10^{-4} k_o (=k_f/K_{OS})$	References
$\text{H}_3\text{Tet}^{3+}$	3.5	-	59
$\text{H}_3\text{Pent}^{3+}$	5.3	-	59
$\text{H}_2\text{Trien}^{2+}$	0.097	-	59
$\text{H}_2\text{Tet}^{2+}$	0.32	-	59
HDien^+	6.2	-	59
HTrien^+	9.3	-	59
HTet^+	13.0	-	59
HPent^+	16.0	-	59
NH_3	4.6	3.6	40
Py	4	3.0	50
Imidazol	5	1.6	52
SCN^-	6	0.6	45
HC_2O_4^-	5	0.3	60
$\text{HO}_2\text{CCH}_2\text{COO}^-$	3	0.16	61
Glycinate^-	15	0.9	52
Diglycinate^-	21	1.2	52
Triglycinate^-	8	0.46	62
$\text{C}_2\text{O}_4^{2-}$	75	0.60	60
$\text{CH}_2(\text{CO}_2)_2^{2-}$	70	0.54	61
$\text{CH}_3\text{PO}_4^{2-}$	280	0.70	63
SO_4^{2-}	-	1.50(at 20°C)	38
NTA^{3-}	2000	-	64

...contd.

Table I.2 (contd.)

HP ₂ O ₇ ³⁻	2100	1.2	65
EDTA ⁴⁻	6000	-	66
HP ₃ O ₁₀	6800	1.2	65
ATP ⁴⁻	4000	1.0	67

between nickel(II) and the incoming ligand.⁵⁵⁻⁵⁷ The rate determining step of overall process is the loss of solvent molecule from the first coordination layer of this outer sphere complex. The general mechanism for octahedral complexes in reactions with a monodentate entering group is



According to this mechanism the rate constant for complex formation

$$k_f = k_o K_{os} / 1 + K_{os} [L^{b-}] \quad \dots (11)$$

which reduces to $k_f = k_o K_{os}$ when $K_{os} [L^{b-}] \ll 1$. When the entering group is a multidentate ligand the Eigen mechanism still holds good. However, a more complicated situation may arise in this case because it can happen⁶⁹⁻⁷⁴ that rate determining step is the chelate ring closure rather than the loss of first solvent

$$k_d = \frac{k_{ro} k_{-o}}{k_{-o} + k_{rc}} \quad (\text{for bidentate})$$

The subscripts to the rate constants k_{rc} and k_{ro} have been introduced to emphasize the ring closure and ring opening processes.

It is apparent from later relationship that the dissociation rate constants k_d in case of bidentate leaving group depends either on opening of chelate ring, where $k_{-o} \gg k_{rc}$ or on rupture of second metal ligand bond, when $k_{-o} \ll k_{rc}$. The dissociation rate constant k_d becomes equal to k_{ro} or $k_{ro} k_{-o} / k_{rc}$ according to whether ring opening or rupture of second metal ligand bond is rate determining. Both these situations have been verified with bi- and also multidentate leaving groups.^{49,59,75,76} It was often found that the bond breakage is the rate determining step. In some cases it has been possible to follow the rupture of nickel ligand bonds of coordinated polydentate ligands.^{77,78} It has also been verified that the rate of dissociation in acid medium decreases as alkyl carbon substitution on a ligand increases.⁸⁴

Some representative dissociation data available on the kinetics of dissociation reactions of octahedral nickel(II) complexes are listed in Table I.3. They have been obtained either directly or from the equilibrium constants of the reactions.^{43,49,51,55,70,76-78,83-88} ($K_{eq} = k_f / k_d$) and the rate constants of complex formation k_f .

Table I.3. Kinetic data for dissociation of nickel complexes in perchloric acid media

System	log k_d	Ref.	System	log k_d	Ref.
Ni(en) ₃ ²⁺	1.95	78	Ni(gly)	-0.27	78
Ni(en) ₂ ²⁺	0.75	78	Ni(2mpa) [*] ₂ ²⁺	-1.5	78
Ni(en) ²⁺	-0.84	78	Ni(2mpa) ₂ ²⁺	-3.5	78
Ni(bn) ₂ ²⁺	-0.59	78	Ni(phen) ₃ ²⁺	-5.11	79,80
Ni(bn) ²⁺	-1.69	78	Ni(phen) ₂ ²⁺	-4.74	79,80
Ni(gly) ₃ ⁻	2.36	78	Ni(phen) ²⁺	-5.0	79,81
Ni(gly) ₂ ⁻	1.32	78	Ni(tet-Meen) ₂ ²⁺	1.25	82

*mpa = 2-methylpyridylamine.

Correlations between the kinetic effects of either the leaving group or the other bonded ligands and extra kinetic parameters have some times been obtained. In this connection, the effect of leaving group is well documented in a series of systematic investigations which have shown that basicity of leaving group is very important in determining the rate of dissociation. For example, rate of dissociation of $\text{Ni}(x\text{-py})(\text{H}_2\text{O})_5^{2+}$ ($x = 3$ and 4-CN, Me, Br, OMe, 3-CONH₂ and 3-NH₃) in acid solution increases with decrease in basicity of the leaving amine according to a linear relationship:⁸⁹ $\log k_d = 1.5 - 0.21 \text{ pK}_a$. A similar type of relationship⁸⁹ has been obtained for dissociation of complexes of the type $[\text{NiL}(\text{H}_2\text{O})_5]^{n+}$, where L is x-phen⁹⁰ or carboxyanion.⁷⁴ The rate of dissociation is

affected by the σ donor ligands while it remains unaffected in presence of σ donor π acceptor ligands. .

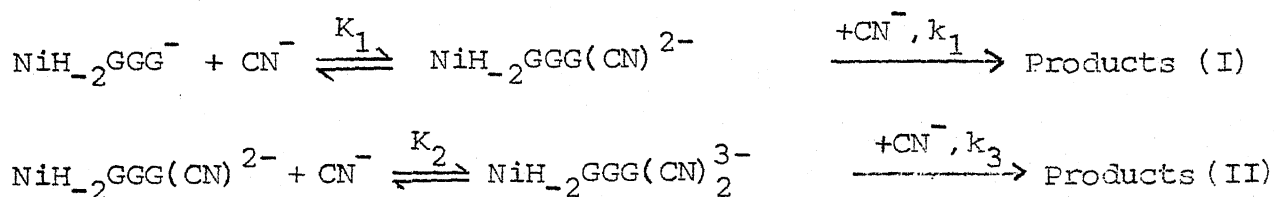
Some more data are now available for the dissociation of nickel(II) complexes involving aminocarboxylates and other ligands.⁹¹⁻⁹⁵ The dissociation of Ni(GEDTA) and other aminocarboxylato nickel(II) complexes⁹³⁻⁹⁵ is through glycinate or ethylenediamine chelate ring intermediate. It is observed that the rate of dissociation of NiHL^{3-n} complex is less in comparison with NiL^{2-n} . Kodama⁹⁵ showed that the ratio of $k_{\text{NiHL}}/k_{\text{NiL}} = 0.36$ while it should be 1.40×10^2 on the basis of Fuoss equation.⁹⁶ This departure suggests the possibility of a hydrogen bond formation between water molecule coordinated to central metal ion and free nitrogen donor atom of GEDTA anion in the reaction intermediate. This internal hydrogen bonding will increase the stability of the intermediate and one will get an enhanced rate constant. This type of hydrogen bonding is not expected in case of NiHL . Generally, it is hard to believe that in the dissociation of nickel(II) aminocarboxylates all three bond breakages are involved in the rate determining step. Furthermore, the nickel-oxygen bond (carboxylate) breakage is much faster than the nickel nitrogen bond (amine) breakage,⁹⁷ so at least nickel-nitrogen-bond should be involved in the rate determining step. Recently the dissociation of $\text{NiGGG}(\text{CN}^-)$ has been reported⁹⁸ and its dissociation rate is found to be 38000 times slower than $\text{NiGGG}(\text{H}_2\text{O})$.⁹⁹ The rate equation given is same as observed for other systems also:^{22, 100-102}

$$\frac{-d[\text{Ni}(\text{GGG})(\text{CN}^-)]}{dt} = \{k_d + k_H [\text{H}^+]\} [\text{NiGGG}(\text{CN}^-)] \quad \dots (14)$$

I.3.5 Monodentate Ligand Exchange Reactions

A typical feature of this kind of reactions is the rupture and formation of several nickel ligand bonds. A common characteristic of these reactions is the observation that they proceed through formation of mixed ligand complex intermediates, in which the central metal ion is simultaneously bonded to both leaving and entering ligands. The rate determining step of overall reaction is cleavage of any one of several bonds between Ni^{2+} and the leaving group which must be broken in the course of reaction. The rate determining step is not necessarily the cleavage of first bond and formation of the mixed ligand complex. The kinetics and mechanism of exchange of unidentate and multidentate ligands by unidentate ligands has been investigated in some detail.^{31-35, 103-116} Cyanide ion is capable of displacing aminocarboxylates from their $\text{Ni}(\text{II})$ complexes.^{31, 32, 106-111} In these complexes Ni^{2+} , which is in high spin state, changes to a low spin state in the product viz., $\text{Ni}(\text{CN})_4^{2-}$. The general mechanism for this class of replacement reactions requires that three cyanides are bonded to Ni^{2+} in the rate determining step. Mixed ligand complex formation is verified as in some other cases.^{117, 118} A multistep mechanism for all these reactions is proposed. At lower pH, HCN is shown to be a reacting species in addition to cyanide. Intramolecular proton transfer from

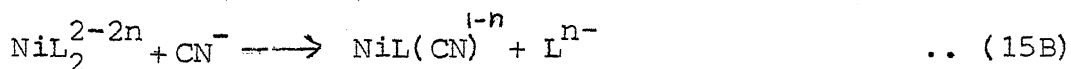
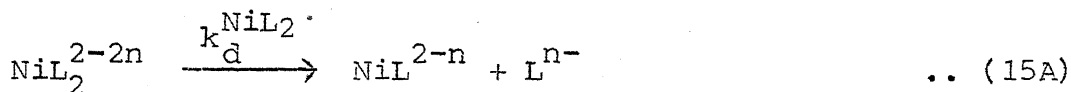
HCN to the more basic nitrogen of the unfolding glycinate occurs.^{31,32,109,110} Stara and Kopanica¹¹¹ proposed a mechanism in which the fourth step was considered to be rate determining in the formation of $\text{Ni}(\text{CN})_4^{2-}$. This conclusion has been shown to be erroneous in a recent publication from this laboratory and reasons have been advanced to justify this conclusion.¹¹³ However, the fourth step is the rate determining one in case of $\text{Ni}(\text{CN})_4^{2-}$ formation from $\text{Ni}^{2+}(\text{aq})$ and NiTrien .¹⁰³⁻¹⁰⁵ The reaction of cyanide ion with $\text{Ni}(\text{TG})$,¹¹² on the other hand, proceeds through a two path mechanism, both involving the formation of mixed ligand complexes. The presence of cyanide in the mixed complex $\text{NiH}_2\text{GGG}(\text{CN})^{2-}$ increases the kinetic stability of the imide group because the cyanide is capable of labilizing the trans imide group which in turn increases the rate. The mechanistic scheme proposed for this reaction¹¹² is given below:



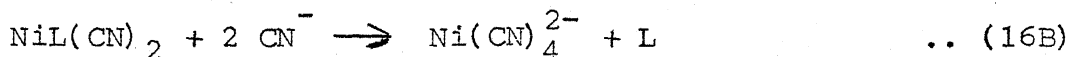
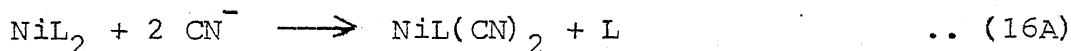
In this reaction there is no change in the spin state and two cyanides are present in the rate determining step for path I. Comparison of these systems indicates that when the rate determining step involves fewer cyanides, no change in spin state takes place.

¹¹¹
Stara and Kopanica reported that the binuclear Ni_2TTHA complex also reacts with cyanide through formation of mixed

ligand complexes. On the other hand complexes of IDA and MIDA react with cyanide according to the following scheme:



followed by the more rapid conversion of the mono complex to $\text{Ni}(\text{CN})_4^{2-}$. Very little is known about the reactions of square planar complexes of Ni(II) with cyanide. Billo¹¹⁴ and Pearson¹¹⁵ et al. have investigated the reaction of cyanide with the square planar complexes of Ni(II) with 1,5-diazacyclooctane (dacco) and dithiooxalate (dto) respectively. Both reactions proceed through formation of very stable mixed ligand complexes. This reaction proceeds in two different steps:



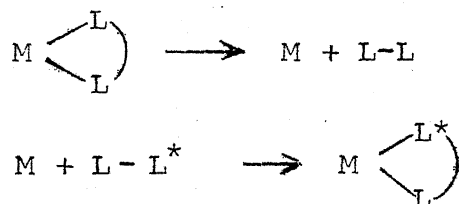
where L represents the above mentioned ligands. This type of mixed ligand complexes were observed in some previous studies also e.g., dithiooxalate¹¹⁷ and 1,10-phen^{116,118} complexes of Ni^{2+} . The reaction of cyanide with the cation $\text{Fe}(\text{L-L})_3$ (where L-L is 1,10-phen¹¹⁹ or a substituted phen,^{120,121} Schiff's base,¹²² bipy,¹²³⁻¹²⁶ or substituted bipy¹²⁷) proceeds in the same way initially forming mixed ligand complexes $\text{Fe}(\text{L-L})_2(\text{CN})_2$. Further reaction of $\text{Fe}(\text{L-L})_2(\text{CN})_2$ is very slow. The formation of

Schiff base complexes follows a simple second order rate law, but for analogous phen compounds the rate law is:

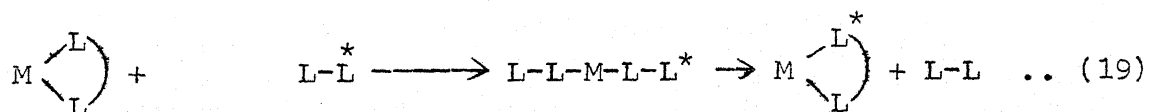
$$-d[\text{Fe(phen)}_3]/dt = \{k'_1 + k'_2[\text{CN}^-]\} [\text{Fe(phen)}_3] \quad \dots (17)$$

I.3.6 Multidentate Ligand Exchange Reactions

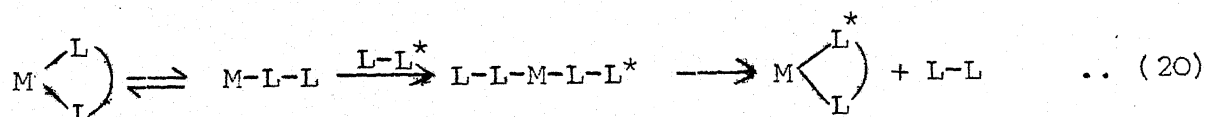
There are three or four mechanisms in vogue for this type of reactions. In the first mechanism the outgoing ligand (L-L) representing any multidentate ligand is completely dissociated from metal (M) before association between M and incoming ligand (L-L*) starts.



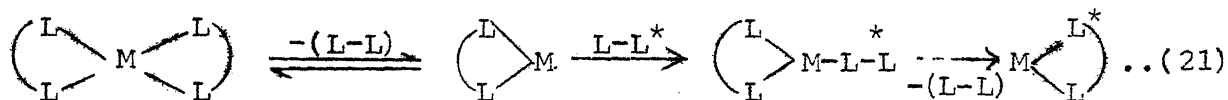
Alternatively, association of metal cation with the incoming ligand may begin before dissociation of outgoing ligand is complete. In this mechanism there will thus be an intermediate in which both ligands are bonded to the metal ion:



A variation of this mechanism is the case of pre-equilibrium partial dissociation of the starting complex:



There is another modification of this scheme which can apply when two multi- e.g., terdentate ligands are replaced by one multi- such as quinquid- or sexidentate ligands:



Kinetic results of multidentate replacement reactions are summarized in Table I.4. It is possible to classify the mechanism of these reactions according to the above equations (18-21). In Table I.4 the dissociation mechanism of Eqn.(18) is represented by D, the dissociation association mechanism of Eqn. (19) by DA and preequilibrium dissociation followed by association mechanism of Eqns.(20) and (21) by QDA. It is often very difficult to distinguish between DA and QDA mechanisms.

Some more examples which follow this type of reaction mechanism involving Ni(II) polyamine complexes are also included in Table I.4. The reaction of NiDGEN with EDTA¹³⁸ follows two paths simultaneously. In path I the dissociation is rate determining and EDTA attack is quite fast while in another path the EDTA adds to NiDGEN and simultaneous bond making and bond breaking is involved in the rate determining step.

Octahedral nickel(II) complexes in which the ligand occupy all six coordination sites usually undergo substitution through the cleavage of one or more metal ligand bonds before the incoming ligand enters the coordination sphere. Complexes of this kind and with formula NiL_2 are usually found to loosen one

Table I.4. Classification of Multidentate ligand exchange reactions

Complex	Incoming Ligand	Type of Mechanism	Ref.
Ni(II) -en	CDTA ⁴⁻	DA	128
Ni(II) -dien	CDTA ⁴⁻	DA	128
Ni(II) -dien	DTPA ⁵⁻	DA	128
Ni(II) -dien	EDTA ⁴⁻	DA	129, 130
Ni(II) -dien	HEEDTA ³⁻	DA	130
Ni(II) -dien	TTHA ⁶⁻	DA	131
Ni(II) -dien	Bipy	DA	132
Ni-dien	Phen	DA	132
Ni-dien	Terpy	DA	132
Ni-dien	Cal	DA	133
Ni-glu	Cal	DA	133
Ni-Asp	Cal	DA	133
NiH ₂ ^{GGG}	en	DA	134
"	N, N' -diMeen	DA	134
"	N, N -diMeen	DA	134
"	dien	DA	134
"	trien	DA	134
"	MIDA	DA	134
Ni-trien	1,10-Phen	DA	135
Ni-trien	EDTA ⁴⁻	?	136
Ni-tet	EDTA ⁴⁻	?	136
Ni-tet	TTHA ⁶⁻	?	137
Ni-DGEN	EDTA ⁴⁻	?	138

...contd.

Table I.4 (contd.)

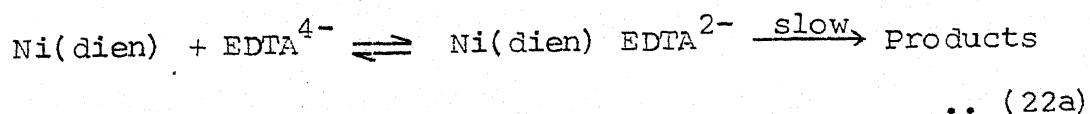
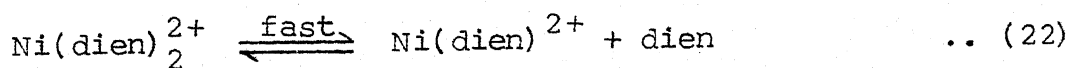
Ni-EDTA	EDTA ⁴⁻	DA	139
Ni-EDTA	Cal	D	140
Ni-EDTA	EBT	DA	141
Ni-EDTA	1, 2-PDTA	DA	142
Ni-EDDA	PAR	DA	143
Ni-EDDA	EDTA	DA	144
Ni-EDMA	DTPA	DA	128
Ni-EDMA	EDTA	DA	130
Ni-EDMA	HEEDTA	DA	130
Ni-EDMA	TTHA	DDA	131
Ni-HEEDTA	Cal	D	140
Ni-HEEDTA	EBT	DA	145
Ni-HEEDTA	EDTA	DA	146
Ni-HEEDTA	DTPA	DA	147
Ni-HEIDA	CDTA	QDA	146
Ni-HEIDA	EDTA	QDA	146
Ni-HEIDA	DTPA	QDA	148
Ni-NTA	DTPA	QDA	146
Ni-NTA	PAR	DA	143
Ni-NTA	EDTA	D, DA	149
Ni-NTA	HEEDTA	D, DA	149
Ni-NTA	TTHA	D, DA	131
Ni-NTA	EBT	DA	141
Ni-NTA	DTPA	DA	146
Ni-NTA	1, 2-CDTA	D, DA	147

...contd.

Table I.4 (contd.)

Ni-IDA	EDTA	?	151
Ni-IDA	1,2-CDTA	?	151
Ni-IDA	DTPA	QDA	156
NiCDTA	EBT	?	152
Ni-DTPA	EBT	?	152
Ni-GEDTA	EBT	DA	145
Ni-TDA	CDTA	D	153
Ni-TDA	EDTA	DDA	153
Ni-NDAP	EDTA	DDA	153
Ni-NDAP	EDTA	DDA	153

ligand L before the entering group participates in the reaction. For instance, the reactions of Ni(dien)_2^{2+} with EDTA^{4-129} and calmagite¹³³ involve preliminary release of one molecule of dien and subsequent attack of EDTA^{4-} or calmagite to Ni(dien) according to the following equations:



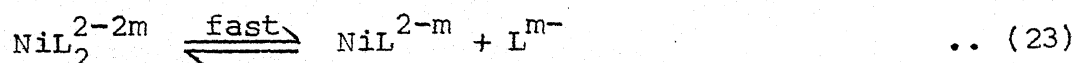
The replacement of one ligand of EDTA family by another presents some interesting features. Such ligand exchange or replacement can occur by a completely or a partially dissociative

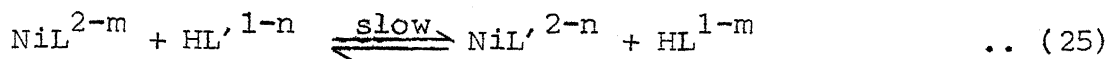
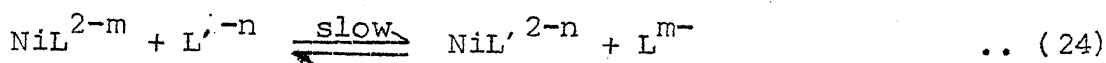
process. A few such systems have also been listed in Table I.4. It is difficult to pick out general reactivity trends from the assembled results. The partial dissociation path (DA) is subject to steric discouragement, e.g., complexes of CyDTA often react only by a complete dissociation path. The importance of steric factors is also illustrated by trien and Me_4trien as entering ligands.¹⁵⁴ Carr et al.¹⁵⁵ have postulated this type of steric difference in case of reactivity of EDTA and 1,2-PDTA. The relatively greater stability of five membered in comparison to six membered chelate rings (as from aspartate) is also reflected in rates of ligand replacement.¹⁵⁶

The effect of addition of other ligands on this type of reactions has been investigated for the replacement of EDTA complexed to Ni(II) by Eriochrome Black T. Here added ammonia or thiocyanate inhibit the reaction by forming mixed ligand chelate of higher stability.^{146,157}

The reaction pathways as found in case of bis complex of dien involving release of ligand as a fast step have been also found in several other reactions of this kind of complexes (NiL_2)^{130,141,150,151,156} with multidentate aminocarboxylates as entering ligands.

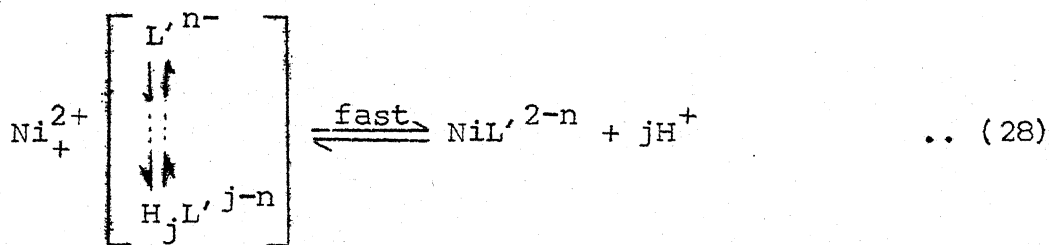
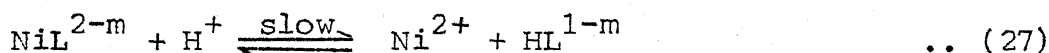
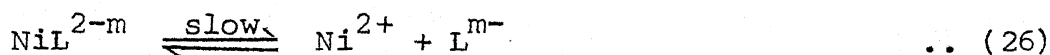
In these cases the reaction rates are found to be strongly affected by acidity of medium according to a rate law which is satisfactorily accounted for by the following reaction scheme:





Pathways (24-25) are also found to occur for ligand substitution of several monoligand nickel(II) chelates of the type NiL .^{141,145,152,153}

It has already been pointed out that the reactions reported above involve mixed ligand complexes as reaction intermediates. This is because the incoming ligand enters the first coordination sphere of Ni(II) before the substrate has fully released its ligands. However, some solitary examples are also reported in literature where the complex fully dissociates before the incoming ligand can coordinate to Ni(II).^{147,153,177,183} The scheme can be represented as below:



I.3.9 Important Factors Influencing Rates and Mechanism

(A) Rates of substitution cover a wide range and may depend on one or more of the following variables:

- i) the charge number of the metal,

- ii) the electronic configuration of the metal ion,
- iii) the nature and geometrical arrangement of ligands,

iv) the solvent and influence of steric hindrance on the reaction. These influences have been treated in some excellent reviews.^{174,175} Only some more interesting features that pertain to aminocarboxylate and polyamine complexes are being included in this discussion.

(B) Behaviour of protonated ligands: The reactivity of mono-, di- or multiprotonated ligands may change some times drastically compared to unprotonated ligands. For example, protonation of free end of Ni-L-L^{2+} fragment could slow down the ring closure¹⁵⁸ and therefore, the observed reaction rate. Another plausible reason is that the presence of protons may drastically reduce the concentration of a reactive exchanging ligand at pH below its pK_a value. The possibility where proton completely blocks a coordination site is also attractive. For example, monoprotonated forms of bipyridyl and phenanthroline react abnormally slowly with nickel complexes. This can not be explained by simply involving lower value of K_{OS} but perhaps represents the physical difficulty of nickel species getting at the blocked nitrogen donor site and lowering the value of k_2 in Equation (5). A very striking example of the effect of protonation on reaction rates is provided by aminocarboxylates and aminoacid amides which react 10^4 times slower than do the protonated species.^{158,159} Whereas the inactivity of $^+\text{NCH}_2\text{COR}$ may be due to sterically

hindered substitution, the lack of activity of zwitter ion may be accounted by the presence of strong intramolecular attraction which must be broken down before even initial reaction occurs. Some times it is possible to locate a protonation site or infer the nature of bonding from a comparison of rate behaviour of various protonated forms.^{86,159}

(C) Effect of substituents on replacement rates: The rates of polyamine Ni(II) complexes in displacement reactions by water or NH_3 molecules increase monotonically¹⁶⁰⁻¹⁶² as the number of coordinated nitrogen increases. But this behaviour is not followed by aromatic bipy, terpy, or phen substituents.^{49,50,160,163,164-166}

It has been suggested that labilizing influence as a result of electron donor properties of aliphatic nitrogen is apparently neutralized by back π -bonding effect when aromatic rings are involved.^{160,161,166}

The effect of substituents at 5 position of phenanthroline on the reaction of $\text{Ni}(\text{phen-5-X})(\text{H}_2\text{O})_4$ with NTA or dienH^{+135} has been attributed to changes in k_2 of Eqn. 5b, which increases with increasing electron donating character of 5-substituents. It appears that substituents which strengthen the phen-Ni bonding weaken the remaining coordinated water.

(D) The role of solvent in ligand substitution reactions: The kinetics of substitution reactions at metal ions such as Ni(II) in aqueous solution depends only slightly on the nature of

ligand and are best described within the framework of I_d mechanism in which rapid formation of an outer sphere complex precedes the rate determining step which is loss of a solvent molecule from inner coordination sphere of metal ion.

In nonaqueous media a wide variation of kinetic behaviour is encountered. It becomes necessary to include additional features to the simple I_d mechanism to account for the observed ligand dependence. Unlike most monodentate ligands whose behaviour is comparable to that in aqueous solution, certain polydentate ligands either react very fast or very slow compared to unidentate ligands in the same solvent. The reaction of 2,2',2''-terpy¹⁶⁷⁻¹⁶⁹ with nickel(II) in DMSO is 60 times slower while that of 5,6-dimethylphenanthroline¹⁷⁰ in acetonitrile is 70 times faster at 25°C compared to the "norm" established by monodentate ligands.^{168,171-173}

In an excellent review on the topic, Coetzee¹⁷⁴ generalized that behaviour in DMSO is typical of strong donor solvents while that in acetonitrile of weak donor solvents. Coetzee¹⁷⁴ also proposed that both the stability of outer sphere complex and the orientation of ligand in outer sphere complex are important factors. Both factors are influenced by

a) the effective positive charge on metal ion, which in turn is determined by donor strength of the solvents;

b) the interaction distance between the ligand and metal ion which again is governed by the thickness and openness of the

inner sphere complex and steric requirements of ligand, and

c) competition between the ligand and solvent in the outer sphere complex. In evaluating the last factor any specific interaction e.g., hydrogen bonding between the ligand and polarized solvent molecule should be carefully considered.

Langford and Tong¹⁷⁵ developed a different approach to solvent effects in kinetics of reactions slower than the diffusion controlled ones. According to them solvent effects can be partitioned into those relating to the encounter equilibria and those relating to rate process. The temptation to discuss this approach in detail is being resisted.

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CHAPTER II

KINETICS AND MECHANISM OF TETRACYANONICKELATE FORMATION FROM MONO(AMINOCARBOXYLATO)NICKEL(II) COMPLEXES

ABSTRACT

The kinetics and mechanism of a system $\text{NiL}^{2-n} + 4 \text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-} + \text{L}^{n-}$, where L = aminocarboxylates viz., TMDTA (trimethylenediamine tetraacetic acid); 1,2-PDTA (1,2-diaminopropane tetraacetic acid); DTPA (diethylenetriamine pentaacetic acid) and TTHA (triethylenetetramine hexaacetic acid) have been investigated. The reaction conditions are $\text{pH} = 11.0 \pm 0.2$, $\mu = 0.1 \text{ M}$ and $\text{temp.} = 25^\circ\text{C}$. The rate of formation of $\text{Ni}(\text{CN})_4^{2-}$ is first order in nickel(aminocarboxylate) complex concentration and varies from 1 to 2 in $[\text{CN}^-]_T$ depending upon the level of cyanide concentration and nature of aminocarboxylate ligand. The formation of mixed ligand complexes of $\text{NiL}(\text{CN})_x^{2-n-x}$ type has been verified. The transition between NiL^{2-n} and $\text{Ni}(\text{CN})_4^{2-}$ is kinetically controlled by presence of three cyanide ions around one nickel ion in the rate determining step. The reaction rates are convenient to follow spectrophotometrically. The reverse

reaction is forced only in presence of large excess of ligand and is first order each in $\text{Ni}(\text{CN})_4^{2-}$ and ligand, and inverse first order in cyanide. From pH profiles for forward reactions it is inferred that between pH 7 to 9 one molecule of HCN is involved in the reaction in addition of two CN^- upto the rate determining step. In the reverse rate studies NaL^{-n+1} complex produced due to presence of NaClO_4 added for ionic strength control was found to be a reacting species. A correlation between the reverse rate constants and K_{NaL} has been established. For forward reactions a LFER is set up between the forward rates and the overall stability constants of the mixed ligand complex intermediates.

II.1 General

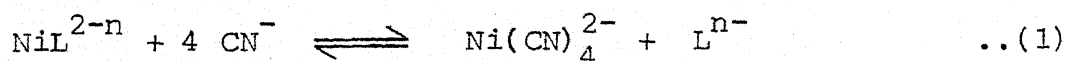
The present investigation deals with the study of some reactions involving interconversion of some octahedral high spin paramagnetic complexes of Ni(II) with aminocarboxylates to a stable diamagnetic low spin square planer complex $\text{Ni}(\text{CN})_4^{2-}$ ($\beta_4 = 10^{30.4}$). The aminocarboxylates chosen for this purpose belong to the EDTA family and are TMDTA (trimethylenediamine tetraacetic acid); 1,2-PDTA (1,2-diaminopropane tetraacetic acid); DTPA (diethylenetriamine pentaacetic acid) and TTHA (triethylenetetramine hexaacetic acid).

At the outset it would be pertinent to recall the behaviour and properties of the cyanide ion in the formation of complexes with transition metal ions. Cyanide ion lies at

halide ions. As a characteristic π bonding ligand, it favours to form mixed ligand complexes with other π bonding ligands. A peculiar class of mixed ligand complexes is one in which the simultaneous coordination of different isoelectronic ligands viz., CN^- , CO , NO^+ , N_2 and C_2^{2-} should be considered. The cyano carbonyl and cyano nitrosyl complexes are well known. The formation of tetracyano nickelate(II) from complexes of Ni(II) aminocarboxylates and polyamines takes place through the formation of mixed ligand complex intermediates of the type $\text{NiL}(\text{CN})_x^{2-n-x}$ where L^{n-} denotes either an aminocarboxylate or a polyamine. Spectrophotometric and kinetic evidence is provided in this work to establish the presence of these mixed complexes during the course of reaction.

II.2 INTRODUCTION

A considerable amount of data is now available on the formation of tetracyano nickelate from $\text{Ni}^{2+}(\text{aq})$,^{1,2} amino-carboxylato nickel(II)³⁻⁸ and to a lesser extent from polyamine-nickel(II) and with other complexes.¹⁰⁻¹³ The formation of tetracyano nickelate(II) from $\text{Ni}^{2+}(\text{aq})$ ^{1,2} is very rapid while its formation by reaction (1) is quite slow when L is EDTA,¹ EGTA, HPDTA, HEEDTA,³ EDDS⁷ and TTHA⁸ and very fast when L is EDDA, NTA³ and trien⁹:



In this work the kinetics and mechanism of reaction (1), both forward and reverse, have been investigated, where L is TMDTA, 1,2-PDTA, DTPA and TTHA. The last reaction which had earlier been studied by Stara and Kopanica⁸ has been reinvestigated. The formation of mixed ligand complexes of $\text{NiL}(\text{CN})_x^{2-n-x}$ type is typical, where x may be 1 or 2. The rate of forward reaction is dependent upon the cyanide ion concentration and is inversely proportional to the stability constant of NiL^{2-n} complexes. The structures of aminocarboxylates and stability constants of their NiL^{2-n} complexes are given in Table II.1 and Table II.2 respectively. Experimental results show that three cyanides are

Table II.1. Names and structures of the aminocarboxylates used in the present study

L^{n-}	Name	Structure
TMDTA^{4-}	Trimethylenediamine tetraacetic acid	$\begin{array}{c} \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{NCH}_2\text{CH}_2\text{CH}_2\text{N} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \end{array}$
$1,2\text{-PDTA}^{4-}$	1,2-Diaminopropane tetraacetic acid	$\begin{array}{c} \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{N-CHCH}_2\text{-N} \\ \quad \quad \quad \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{CH}_3 \quad \quad \quad \text{CH}_2\text{COO}^- \end{array}$
DTPA^{5-}	Diethylenetriamine pentaacetic acid	$\begin{array}{c} \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \quad \text{CH}_2\text{COO}^- \\ \quad \quad \quad \diagdown \quad \diagup \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{NCH}_2\text{CH}_2\text{-N-CH}_2\text{CH}_2\text{N} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \diagdown \\ \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \quad \text{CH}_2\text{COO}^- \end{array}$
TTHA^{6-}	Triethylenetetramine hexaacetic acid	$\begin{array}{c} \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \quad \text{CH}_2\text{COO}^- \quad \text{^-OOCCH}_2\text{C} \\ \quad \quad \quad \diagdown \quad \diagup \quad \quad \quad \diagdown \quad \diagup \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N} \\ \quad \quad \quad \diagup \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \quad \quad \diagdown \quad \quad \quad \diagup \quad \diagdown \\ \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \quad \text{^-OOCCH}_2\text{C} \quad \text{CH}_2\text{COO}^- \end{array}$

Table II.2. Protonation constants of aminocarboxylates and stability constants of aminocarboxylatonickel(II) complexes⁺

A. Protonation Constants of Aminocarboxylates (log K)

L ⁿ⁻	K _{HL}	K _{H₂L}	K _{H₃L}	K _{H₄L}	K _{H₅L}	H _{H₆L}	Ref.
TMDTA ⁴⁻	10.56 ^a	8.00 ^a	-	-	-	-	14-18
	10.46 ^b	8.02 ^b	2.57 ^b	1.88	-	-	14-18
	10.27 ^c	7.90 ^c	2.69 ^c	2.00 ^d	-	-	14-18
1,2-PDTPA ⁴⁻	10.86 ^b	6.25 ^b	2.79 ^b	1.83 ^b	-	-	19-23
	10.84 ^d	6.20 ^d	-	-	-	-	19-23
DTPA ⁵⁻	10.56 ^d	8.69 ^d	4.37 ^d	2.87 ^d	1.94 ^d	-	14, 24
	10.46 ^h	8.41 ^h	4.14 ^h	2.70 ^h	2.20 ⁱ	-	14, 24
	9.48 ⁱ	8.26 ⁱ	4.19 ⁱ	2.50 ⁱ	2.50 ⁱ	-	14, 24
TTHA ⁶⁻	10.19 ^d	9.40 ^d	6.16 ^d	4.16 ^d	2.95 ^d	2.42 ^d	24-28

B. Stability Constants of Aminocarboxylatonickel(II) Complexes (log K)

	K _{NiL}	K _{NiHL}	K _{NiH₂L}	K _{NiH₃L}	K _{NiH₄L}	K _{Ni₂L}	K _{Ni₂HL}	K _{Ni₂H₂L}	K _{NaL}	Ref.
TMDTA ⁴⁻	18.15 ^b	2.2 ^b	-	-	-	-	-	-	1.08 ^e	29, 30
	18.07 ^{d*}	-	-	-	-	-	-	-	-	-

..contd.

Table II.2 (contd.)

1,2-PDTA ⁴⁻	19.66 ^f	2.34 ^g	-	-	-	-	2.24 ^b	31-34
	-	-	-	-	-	-	2.55	31-34
DTPA ⁵⁻	20.17 ^d	5.67 ^d	3.02 ^d	5.59 ^d	-	-	(1.0) ^e	35,36
	-	5.62 ^d	-	-	-	5.53 ^d	-	-
TTHA ⁶⁻	19.40 ^d	7.98 ^d	4.86 ^d	2.74 ^d	1.15 ^d	13.00 ^d	2.30 ^d	(1.00) ^e 37-41

a) temp = 20°C, μ = 0.10 M (TMAcL); b) temp = 20°C, μ = 0.1 M (KNO₃); c) temp = 20°C, μ = 0.10 M (NaNO₃); d) temp = 25°C, μ = 0.1 M (KNO₃); d*) The value at 25°C for log K_{NiL} can be calculated from the reported value at 20°C of ΔH° = -6.66 kcal, ΔS° = 60.3 e.u. and $\log K_{\text{NiL}}$ = 18.15 (ref.2); e) temp = 25°C, μ = 0.5 M (adjusted by KNO₃ and NaNO₃); f) temp = 25°C, μ = 0.2 M (KNO₃); g) temp = 25°C, μ = 1.0 M (KNO₃); h) temp = 20°C, μ = 1.0 M (TMAcL); i) temp = 20°C, μ = 1.0 M (NaClO₄). values without superscript are for t = 25°C, μ = 0.1 M (NaClO₄).

+The terminology used for these constants is consistent with the convention used by Bjerrum et al. (cf. J. Bjerrum, G. Schwarzenbach and L.G. Sillen, "Stability Constants: pt.I, Organic Ligands", The Chemical Society (1957)).

required around the central nickel ion to bring about the rate determining step. The fourth cyanide adds very rapidly and displaces the remaining glycinate segment of the ligand finally producing $\text{Ni}(\text{CN})_4^{2-}$.

II.3 EXPERIMENTAL SECTION

Reagents

All reagents used in these investigations were of AR grade unless otherwise stated. Synthesis of TMDTA was tried by a method described by Schwarzenbach and Ackerman⁴² and another described by Tanaka and Ogino,⁴³ but a crystalline product could not be obtained. The ligand was prepared finally by an excellent method described by Weyh and Hamm⁴⁴ and a good yield of H_4TMDTA was obtained. The crude product was recrystallized twice from ethanol-water mixture and dried at 105°C . 1,2-PDTA, DTPA and TTHA were obtained from K & K Labs. (U.S.A.), Geigy Lab. (U.S.A) and Sigma Chemical Co. (U.S.A.) respectively. Microanalysis results of all these ligands including TMDTA of C, H and N agreed very well with calculated values. Doubly distilled deionized water was used to prepare all solutions.

Nickel perchlorate, $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, supplied by Alpha Inorganics (U.S.A.) was recrystallized before use. A stock solution was standardized against EDTA by complexometric titrations.⁴⁵

Sodium perchlorate was obtained from E. Merck (Germany). It was recrystallized before use. A stock solution of 1 M was

prepared by adding 14.05 g of recrystallized $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ to 100 ml solution. NaClO_4 and in some kinetic runs NaNO_3 and KNO_3 were also used for ionic strength control.

Sodium cyanide was obtained from M & B Ltd., Degenham (England). A stock solution of 1 M was prepared and standardized every time before starting the run by titrating against standard AgNO_3 .⁴⁶

Ni(II) complexes of all aminocarboxylates viz., TMDTA, 1,2-PDTA, DTPA and TTHA were prepared by adding slight excess of nickel perchlorate to the standard ligand solution which was standardized by pH metric titrations and removing the excess nickel as hydroxide at pH 11.0 by milipore filtration through a $0.45 \mu\text{m}$ filter. The solutions were allowed to stand in a cold room for two more days and finally filtered through a $0.22 \mu\text{m}$ filter. The clear sparkling solutions were standardized by addition of a ten-fold excess of NaCN at pH 11.0 and after allowing for complete conversion to Ni(CN)_4^{2-} the absorbances were measured at 267 nm ($\epsilon = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and at 285 nm ($\epsilon = 4.63 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) using suitable dilutions.

$\text{Na}_2\text{Ni(CN)}_4$ solution was prepared by mixing exact stoichiometric amounts of $\text{Ni(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and sodium cyanide in aqueous solution.

Apparatus:

Beckman DU and later Toshniwal Spectrometer type RL02 (Beckman DU type) was used for kinetic studies. The temperature

The reaction mixture was maintained at $25 \pm 0.1^\circ\text{C}$ by an ultra-thermostat type 2NBE (GDR). The cell compartment was maintained at constant temperature by a circulatory arrangement of water from the thermostat around the cell compartment. All pH measurements were taken on a Toshniwal pH meter model A type CL-44 or an Elico digital pH meter model LI-120 using BDH standard buffers.

Procedure

The forward and reverse reactions were followed spectrophotometrically by observing the change in absorbance of $\text{Ni}(\text{CN})_4^{2-}$ as a function of time. From Figure II.1 one can see that $\text{Ni}(\text{CN})_4^{2-}$ shows two distinct peaks at 267 nm ($\epsilon = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and at 285 nm ($\epsilon = 4.63 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) while NiL^{2-n} complexes do not absorb appreciably at these wavelengths, but where they do, appropriate corrections were made for this factor. The spectra of NiL complexes in the visible region are given in the Figures II.2 - II.5. The concentration of $\text{Ni}(\text{CN})_4^{2-}$ solution was determined from absorbance data using the Expression (2) where b is the pathlength:

$$\left[\text{Ni}(\text{CN})_4^{2-} \right] = (A_t - A_o) / b (\epsilon_{\text{Ni}(\text{CN})_4^{2-}} - \epsilon_o) \quad \dots (2)$$

A_t is the sum of absorbances of $\text{Ni}(\text{CN})_4^{2-}$ complex and other complex species formed such as $\text{NiL}(\text{CN})^{1-n}$ or $\text{NiL}(\text{CN})_2^{n-}$ at time t , A_o the initial absorbance at zero time. $\epsilon_{\text{Ni}(\text{CN})_4^{2-}}$ represents the molar absorptivity of $\text{Ni}(\text{CN})_4^{2-}$ and ϵ_o of other species present in the reaction mixture.

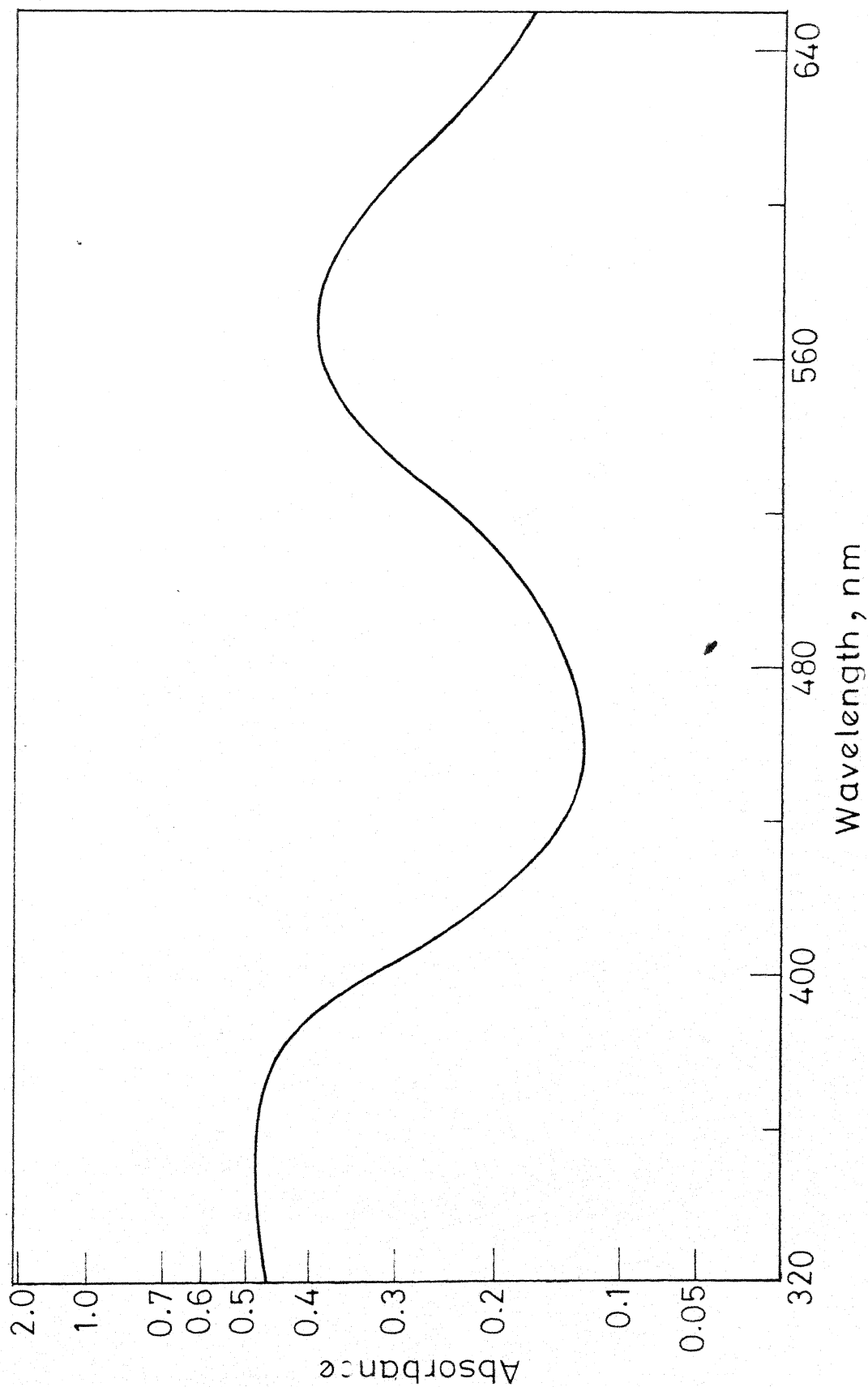


FIG. 17.2 Absorption Spectra of NiTMDTA^{2-} Complex, $[\text{NiTMDTA}] = 7.0 \times 10^{-2} \text{ M}$

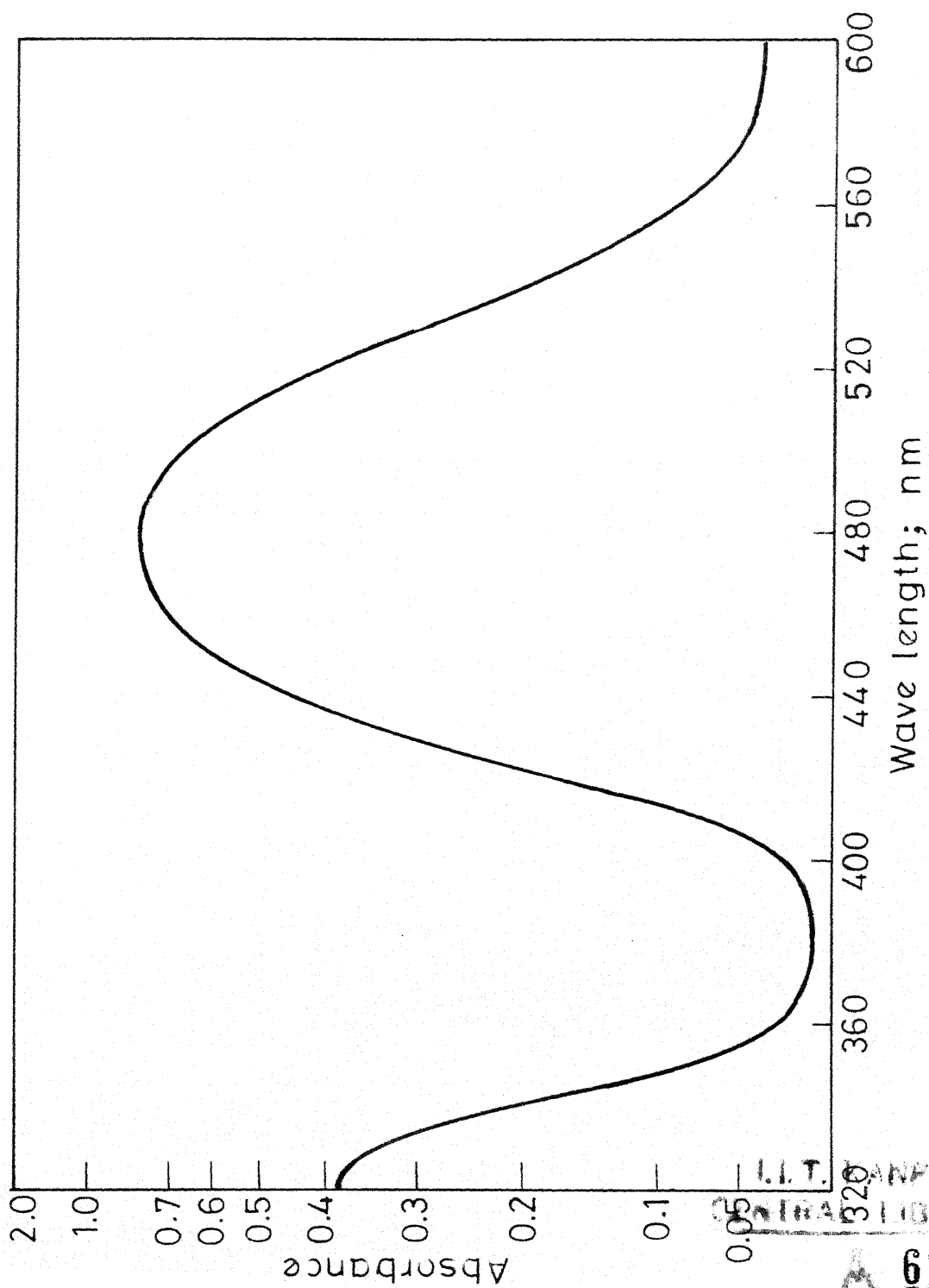


Fig. 11.3 Absorption spectra of Ni-1,2-EDTA complex, $[Ni-1,2-EDTA] = 7.4 \times 10^{-2} M$

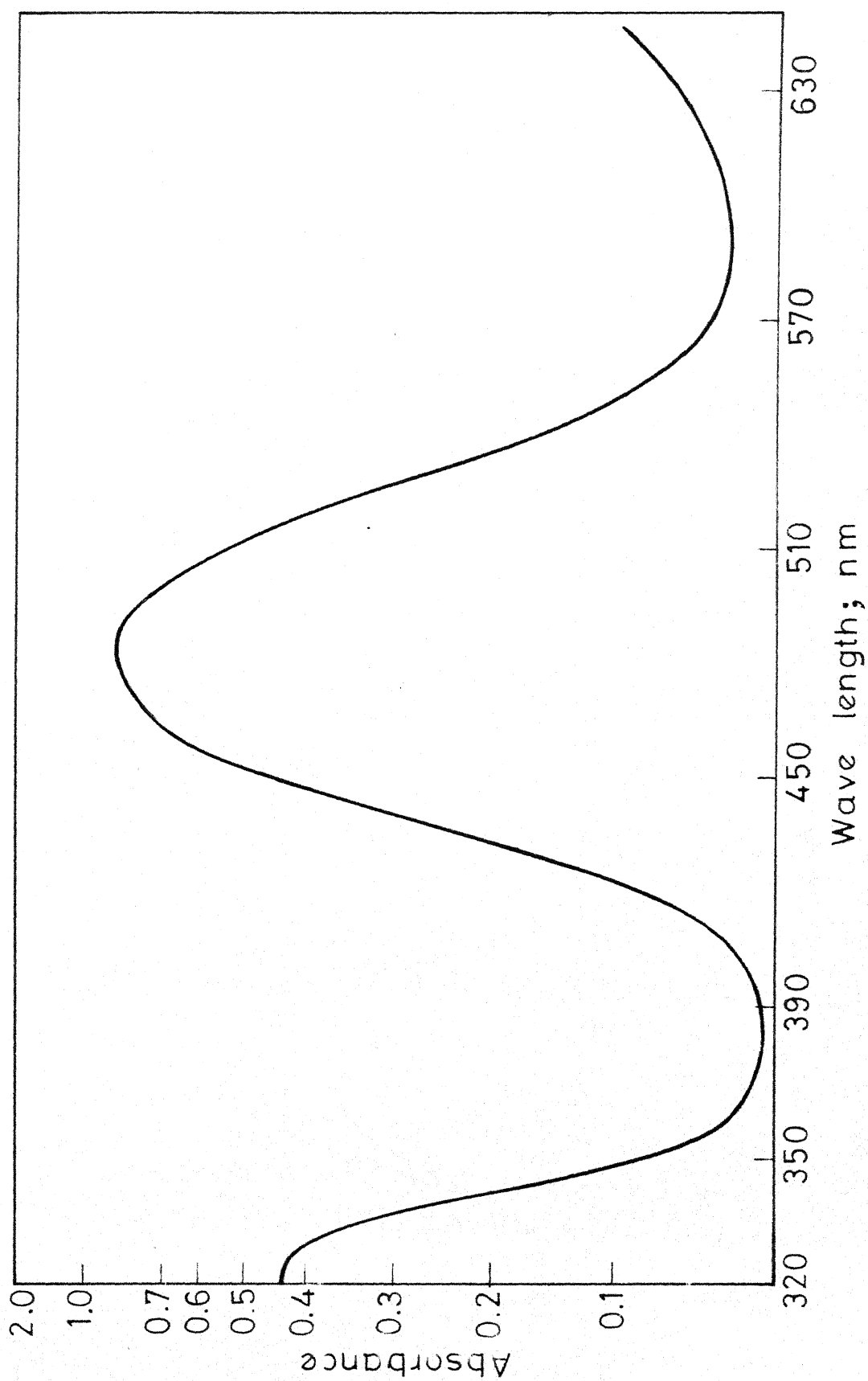


Fig. 11.4 Absorption spectra of NiDTPA^{3-} complex $[\text{NiDTPA}] = 9.70 \times 10^{-2} \text{ M}$

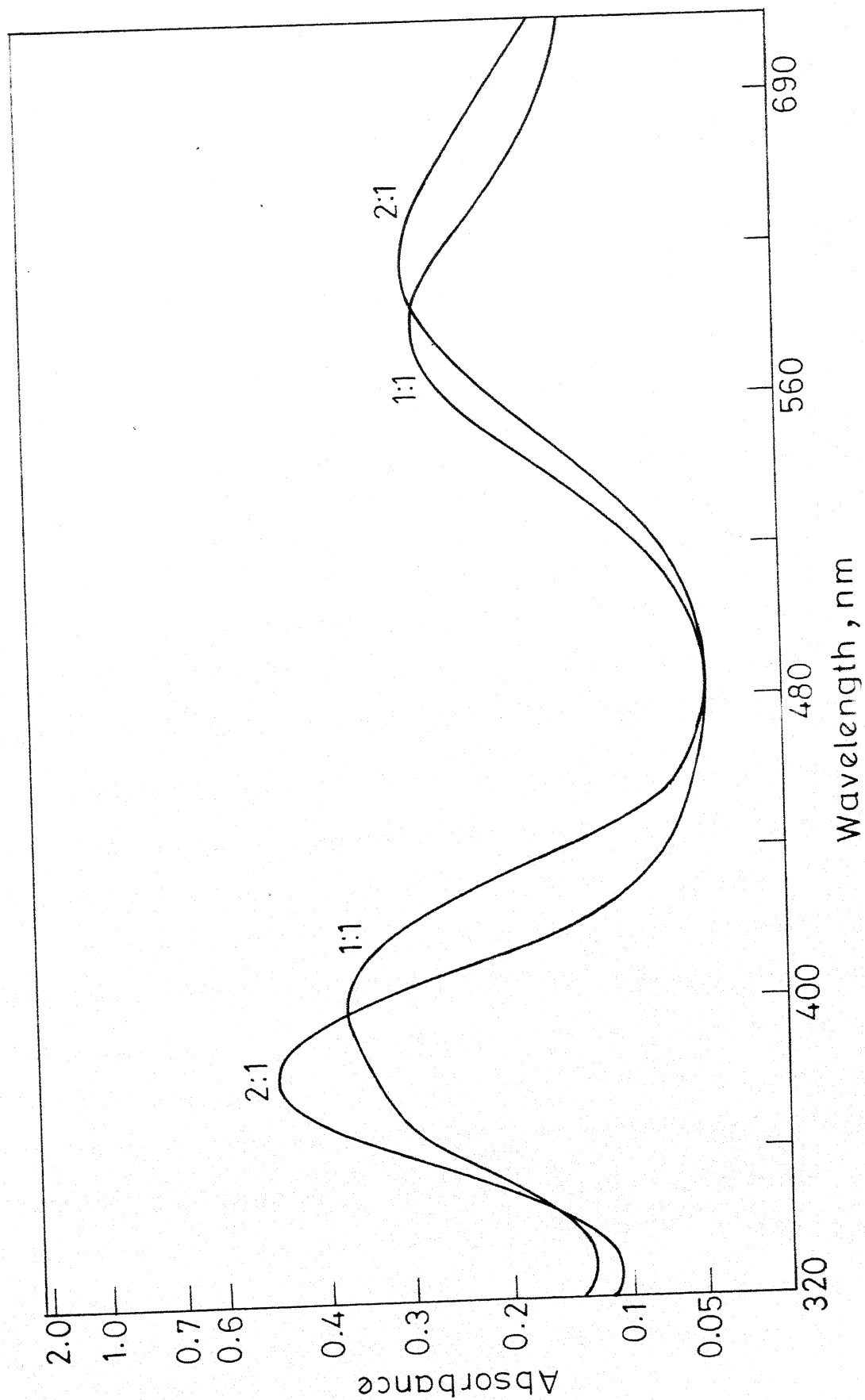


Fig. II.5 Absorption spectra of NiTHA⁴⁻ complex, $[Ni] : [THA] = 7.2 \times 10^{-2} M$

The forward reactions were run with excess cyanide and all gave excellent first order plots. At least triplicate runs were made for each reactant concentration and the rate constants reported herein are averages of these runs. The rate expression with CN^- present in excess is given in (3) where x varies from 1 to 2 depending on the extent of mixed cyanide complex formation.

$$d[\text{Ni}(\text{CN})_4^{2-}]/dt = k_{\text{obsd}}[\text{NiL}(\text{CN})_x^{2-n-x}] \quad \dots(3)$$

The observed first order rate constants were evaluated from the plots of $\log(A_\infty - A_t)$ vs time (Figure II.6 for a specimen). The value of k_{obsd} is dependent on free cyanide ion concentration as well as on the nature of $\text{NiL}(\text{CN})_x^{2-n-x}$. The rate of formation of $\text{NiL}(\text{CN})_x^{2-n-x}$ is fast as compared to the formation of $\text{Ni}(\text{CN})_4^{2-}$ and there is rapid preequilibration with $\text{NiL}(\text{CN})^{1-n}$ & $\text{NiL}(\text{CN})_2^{-n}$.

The pH profile (to be discussed later) for all the four reactions shows no dependence of forward rate constant on pH in the range 10.0-11.5. The majority of the reactions were, therefore, carried out at $\text{pH } 11.0 \pm 0.2$ where the principal reacting species is cyanide ion. The pH of the solution was adjusted by the addition of dilute solutions of Analar NaOH or HClO_4 . No buffers were added for fear of complicating the system. The pH values were corrected for $-\log[\text{H}^+]$ by subtracting 0.11 from recorded pH readings.⁴⁷ The ionic strength of the medium in the forward rate studies was maintained at 0.1 M (NaClO_4) except in few runs in case of 1,2-PDTA and DTPA where rate constants have been reported after applying necessary correction. In the

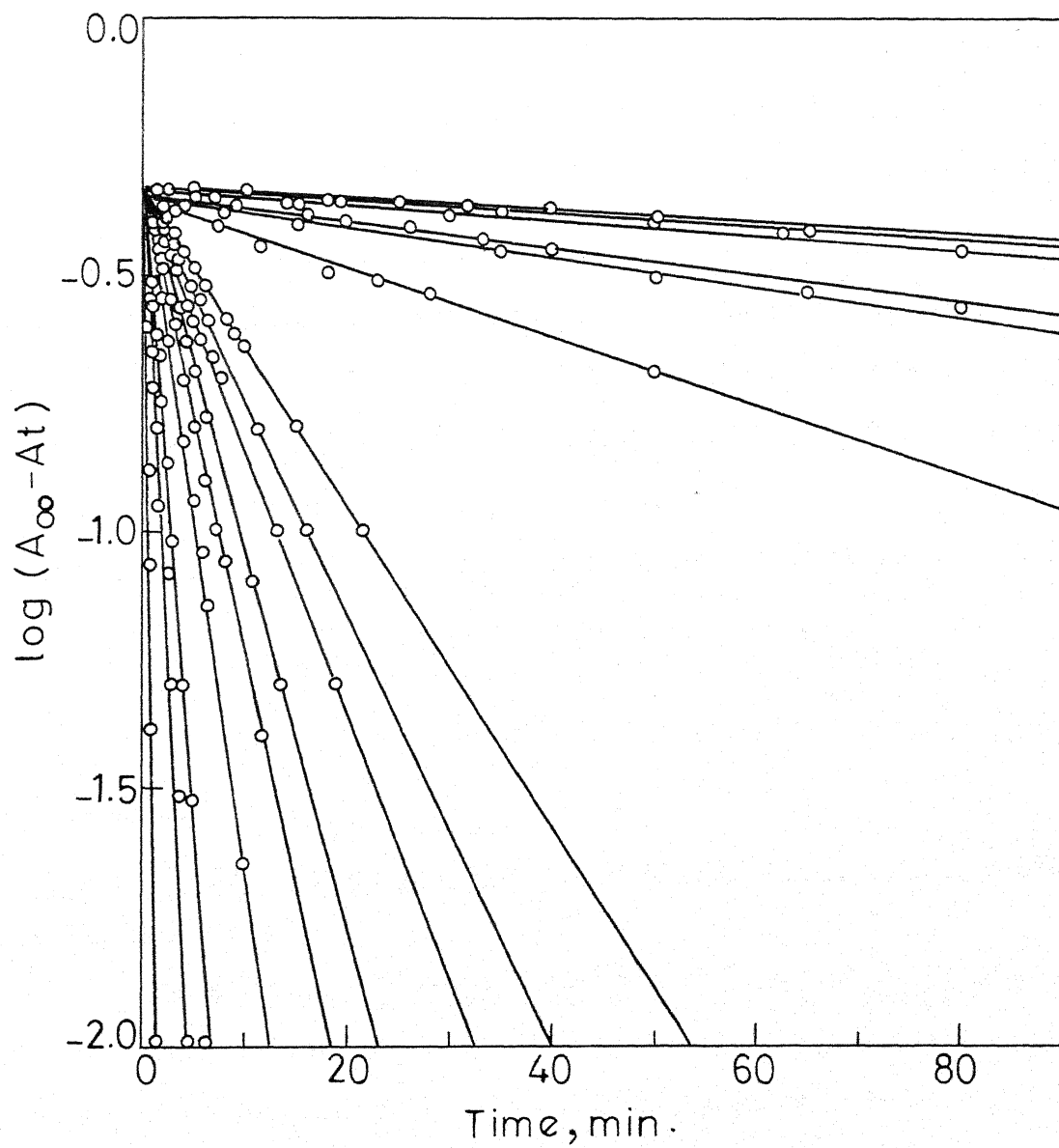


Fig. 11.6 Pseudo First Order Plots for NITINDIA^{2-}
Reaction with Cyanide Ion

form of aminocarboxylate at a specified pH can be calculated by means of equation (4)

$$a_{LH_{n-m}}^{(n-m)+} = \frac{[H^+]^{n-m} K_1 K_2 \dots K_m \times 100\%}{[H^+]^n + [H^+]^{n-1} K_1 + \dots + K_1 K_2 \dots K_m} \quad \dots(4)$$

Where, $m=1,2,3,\dots$ and $n=\text{no. of dissociable protons}$

The values of pK'_a s of ligands and stability constants of complexes used in these calculations are given in Table II.2. The species distribution of complexes can be calculated by an iterative method, beginning with a crude approximation $[M^i] = [M^i]_T$ and using equation (5)

$$[M^i] = [M^i]_T + \sum_{j=1}^{j=n} p_{ij} C_j \quad \dots(5)$$

where p_{ij} is the number of metal ions of M^i in the species j .

The species distribution as a function of pH is shown in Figures II.7 - II.10. This information is necessary for interpretation of kinetic data and particularly for resolution of rate constants pertaining to unprotonated and protonated reactive species.

Kinetics of Forward Reactions

From a look at the stability constants of aminocarboxylato nickel(II) complexes (Table II.2) and β_4 of $Ni(CN)_4^{2-}$ one can infer that all the forward reactions are thermodynamically favoured. All the reactions were carried out in presence of large excess (10 to 2000 fold of Ni(II)) of cyanide i.e., under pseudo first order conditions. During these experiments a

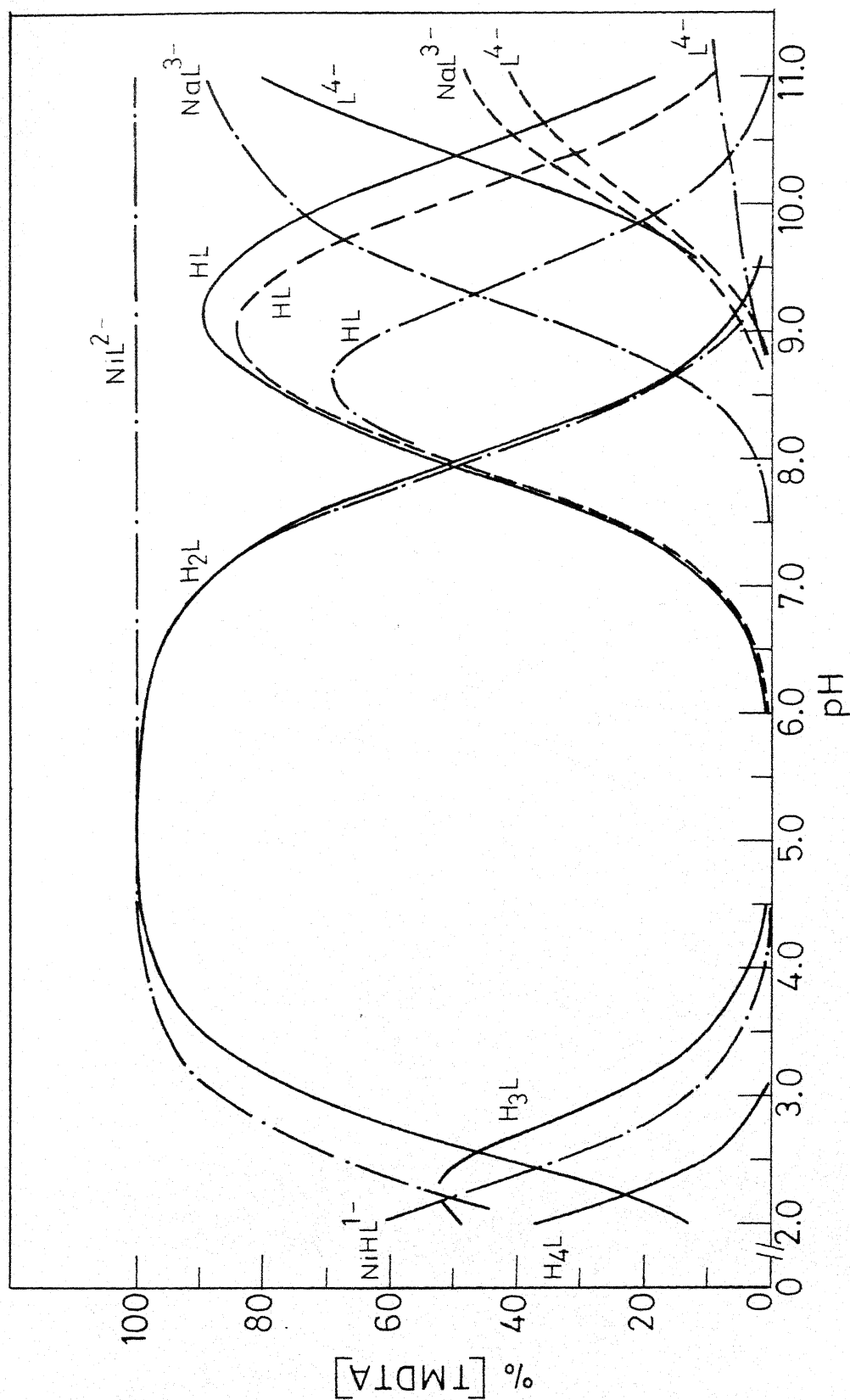


FIG. 11.7 Species distribution of TMDB, NITMDTA and NITMDTA as a function of pH

$[\text{Ni}^{2+}]_T = [\text{TMDB}]_T = 5.0 \times 10^{-4} \text{ M}$

— when only ligand is

--- when ligand and sodium ions are taken $[\text{Na}^+] = 0.1 \text{ M}$

-.- when ligand and sodium ions are taken $[\text{Na}^+] = 0.5 \text{ M}$

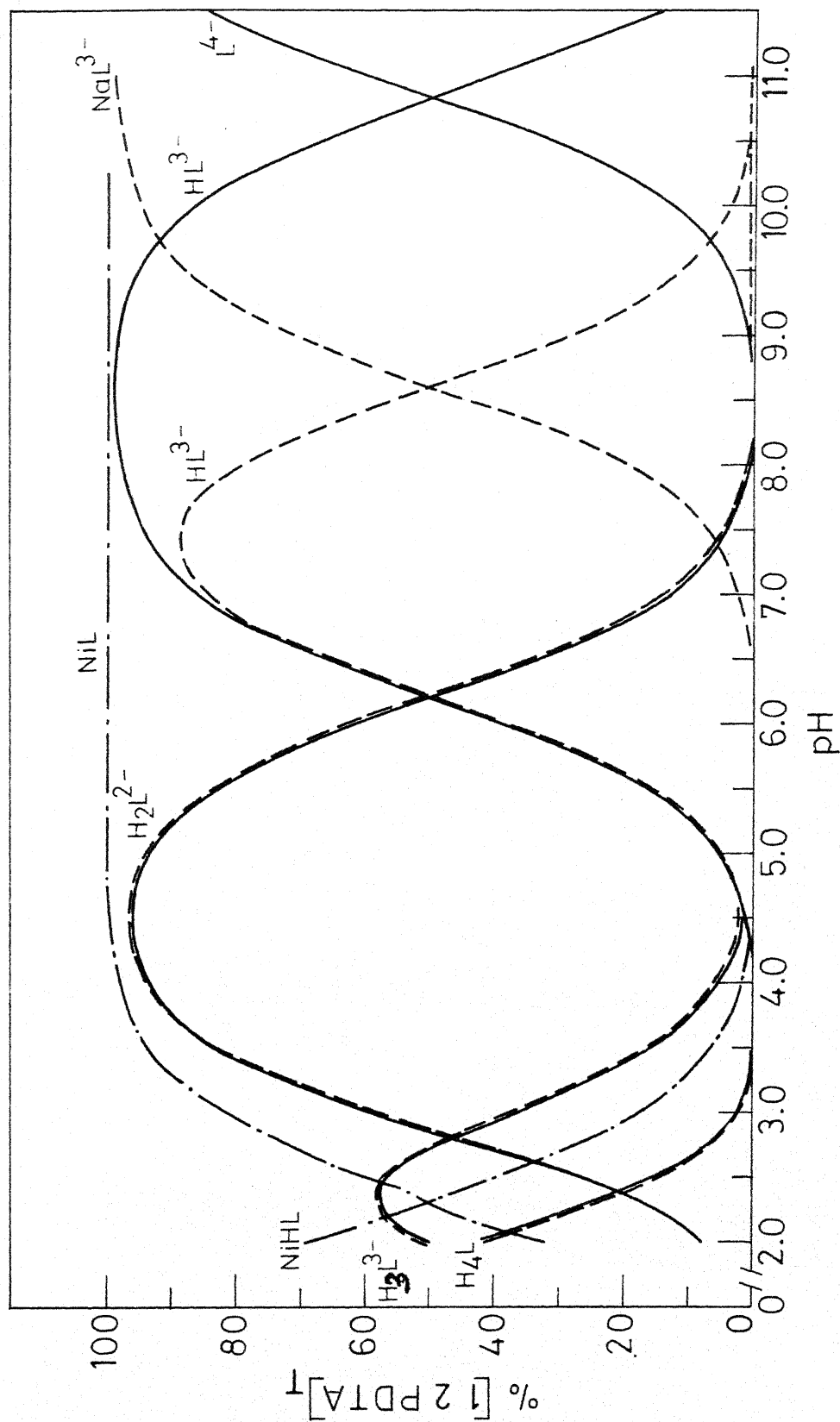


FIG. 11.8 Species distribution of 1,2-PDTA, $\text{Ni}(1,2\text{-PDTA})$ and NiL^{3-} as a function of pH; $[\text{Ni}^{2+}]_T = [1,2\text{PDTA}]_T = 5.0 \times 10^{-4} \text{ M}$

- When only ligand is taken
- When Sodium ion is also taken $[\text{Na}^+]$
- .- When Ni^{2+} and 1,2-PDTA is taken

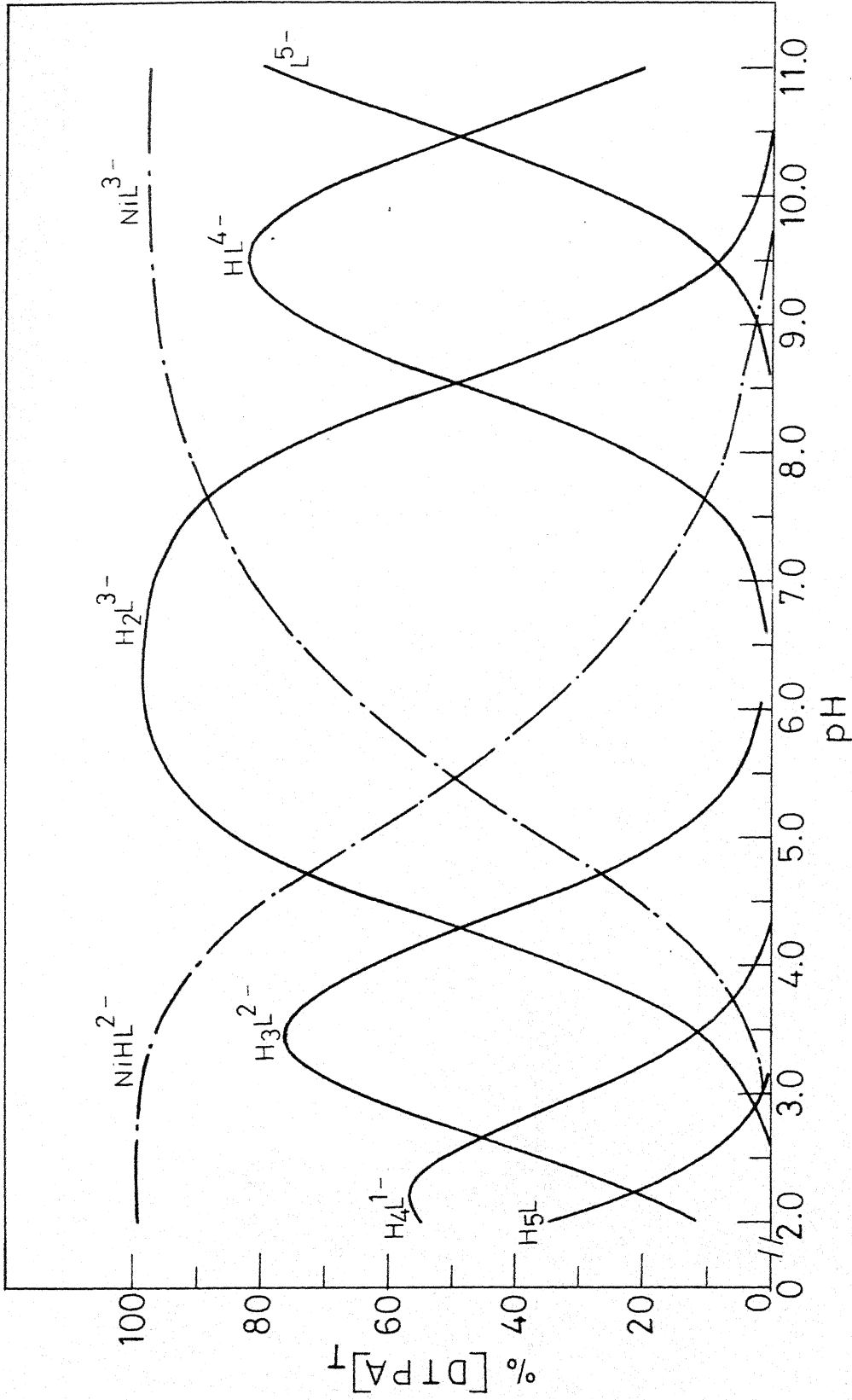


Fig. 11.3 Species Distribution of EDTA and NiEDTA as a Function of pH
 $[Ni^{2+}]_T = [DTPA]_T = 5.0 \times 10^{-4} M$

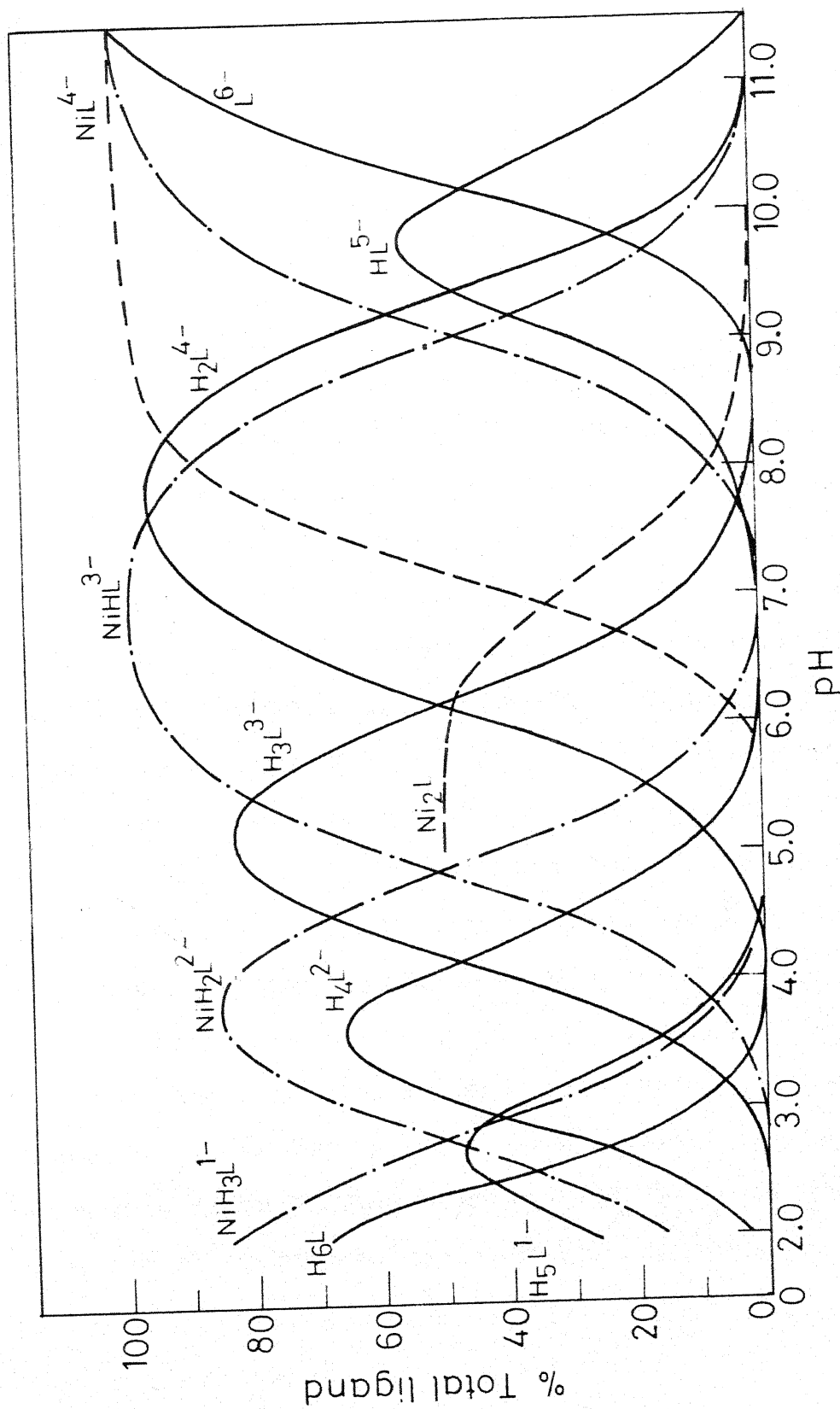


FIG. 11.10 Species distribution of EDTA and NiEDTA as a function of pH

$$[Ni^{2+}] = [L]_T = 5.0 \times 10^{-4} M$$

significant observation made was that a small but instantaneous increase of absorbance takes place as soon as the reactants are mixed which is followed by slow formation of $\text{Ni}(\text{CN})_4^{2-}$. This observation led to the conclusion that some type of mixed ligand intermediates were produced prior to the rate determining step. A similar observation was also reported by Margerum et al.³⁻⁶ and Stara and Kopanica⁸ in similar reactions investigated earlier. The observed psuedo first order rate constants for all the four reactions are given in Table II.3. The term $[\text{CN}^-]_T$ refers to the added cyanide concentration and includes a small amount of HCN that may be present at pH 11.0, as well as a very small fraction of cyanide ion used up in the formation of $\text{Ni}(\text{CN})_4^{2-}$ ($\sim 10^{-5}$ M). The dependence of observed rate constants on cyanide ion concentration can be seen in Figure II.11. The slopes in all cases change from 2 to 1 as cyanide concentration increases. A slope of 3 at lower concentration of CN^- , changing to 2 and finally approaching 1, has been found in case of NiEEDA^0 and NiNTA^{1-} in an earlier work.³ But third order dependence at lower cyanide concentration could not be observed in this work. At such lower concentration where it might have been detected, the rate of reaction becomes too slow to be measured. Stara and Kopanica⁸ have reported only a third order dependence in the NiTTA reaction with CN^- but this observation could not be reproduced here. Their data has been questioned, reinvestigated and reinterpreted in a recent communication⁵² from this laboratory.

Table II.3. Kinetics of formation of $\text{Ni}(\text{CN})_4^{2-}$ from mono(amino-carboxylato)nickel(II) complexes using excess cyanide ion at temp = $25.0 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ M}$ (NaClO_4); pH = 11.0 ± 0.2 .

$[\text{CN}^-]_{\text{T}}, \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$	$[\text{CN}^-]_{\text{T}}, \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$
$\text{NiTMDTA}^{2-}: [\text{NiL}]_{\text{i}} = (1.64\text{--}9.91) \times 10^{-5} \text{ M}.$			
7.00×10^{-4}	4.22×10^{-5}	6.40×10^{-3}	1.31×10^{-3}
1.07×10^{-3}	4.98×10^{-5}	8.00×10^{-3}	1.60×10^{-3}
1.28×10^{-3}	5.05×10^{-5}	9.15×10^{-3}	1.97×10^{-3}
1.60×10^{-3}	8.50×10^{-5}	1.07×10^{-2}	2.78×10^{-3}
2.13×10^{-3}	1.07×10^{-4}	1.20×10^{-2}	3.42×10^{-3}
3.20×10^{-3}	2.53×10^{-4}	1.30×10^{-2}	5.00×10^{-3}
6.40×10^{-3}	1.18×10^{-3}	2.15×10^{-2}	9.37×10^{-3}
6.40×10^{-3}	1.27×10^{-3}	3.20×10^{-2}	1.41×10^{-2}
6.40×10^{-3}	1.30×10^{-3}	6.40×10^{-2}	3.16×10^{-2}
$\text{Ni}(1,2\text{-PDTA})^{2-}: [\text{NiL}]_{\text{i}} = (6.20 \times 10^{-5} \text{--} 2.03 \times 10^{-3}) \text{ M}.$			
1.74×10^{-2}	5.46×10^{-6}	4.34×10^{-2}	3.19×10^{-5}
4.34×10^{-2}	3.30×10^{-5}	1.63×10^{-2}	4.55×10^{-6}
4.34×10^{-2}	3.16×10^{-5}	8.15×10^{-3}	1.19×10^{-6}
2.17×10^{-2}	6.80×10^{-5}	1.36×10^{-2}	3.24×10^{-6}
4.34×10^{-2}	3.31×10^{-5}	1.02×10^{-2}	1.88×10^{-6}
4.34×10^{-2}	3.33×10^{-5}	8.16×10^{-2}	1.39×10^{-4}
4.34×10^{-2}	3.78×10^{-5}	2.72×10^{-2}	1.31×10^{-5}
4.34×10^{-2}	3.62×10^{-5}	1.24×10^{-1}	$(2.89 \times 10^{-4})^a$
4.34×10^{-2}	2.94×10^{-5}	$(\mu = 0.13)$	

...contd.

Table II.3 (contd.)

1.55×10^{-1} ($\mu = 0.16$)	$(7.94 \times 10^{-4})^a$	3.37×10^{-1} ($\mu = 0.34$)	$(1.80 \times 10^{-3})^a$
1.68×10^{-1} ($\mu = 0.17$)	$(1.28 \times 10^{-3})^a$	6.20×10^{-1} ($\mu = 0.62$)	$(2.75 \times 10^{-3})^a$
3.10×10^{-1} ($\mu = 0.32$)	$(1.77 \times 10^{-3})^a$	6.75×10^{-1} ($\mu = 0.68$)	$(4.49 \times 10^{-3})^a$
NiDTPA ³⁻ : $[\text{NiL}]_i = (4.41-5.55) \times 10^{-5}$ M.			
2.20×10^{-3}	4.38×10^{-5}	3.13×10^{-2}	6.53×10^{-3}
4.40×10^{-3}	9.80×10^{-5}	3.75×10^{-2}	1.28×10^{-2}
5.35×10^{-3}	1.69×10^{-4}	5.00×10^{-2}	1.64×10^{-2}
6.68×10^{-3}	2.77×10^{-4}	6.18×10^{-2}	2.27×10^{-2}
8.75×10^{-3}	3.94×10^{-4}	1.20×10^{-1}	$(3.51 \times 10^{-2})^a$
1.07×10^{-2}	6.07×10^{-4}	($\mu = 0.12$)	
2.04×10^{-2}	2.03×10^{-3}	2.48×10^{-1}	$(7.54 \times 10^{-2})^a$
2.68×10^{-2}	3.97×10^{-3}	($\mu = 0.25$)	
Ni(TTHA) ⁴⁻ : $[\text{NiL}]_i = (1.00-9.50) \times 10^{-5}$ M.			
2.25×10^{-4}	6.12×10^{-6}	2.25×10^{-3}	3.91×10^{-4}
4.50×10^{-4}	2.05×10^{-5}	3.00×10^{-3}	3.70×10^{-4}
7.50×10^{-4}	2.23×10^{-5}	4.50×10^{-3}	5.75×10^{-4}
9.00×10^{-4}	1.01×10^{-4}	4.50×10^{-3}	6.10×10^{-4}
9.00×10^{-4}	1.08×10^{-4}	6.00×10^{-3}	8.60×10^{-4}
1.50×10^{-3}	1.63×10^{-4}	9.00×10^{-3}	1.40×10^{-3}
1.80×10^{-3}	2.75×10^{-4}	9.00×10^{-3}	1.25×10^{-3}
1.80×10^{-3}	3.00×10^{-4}	1.80×10^{-2}	2.79×10^{-3}
2.25×10^{-3}	3.35×10^{-4}		

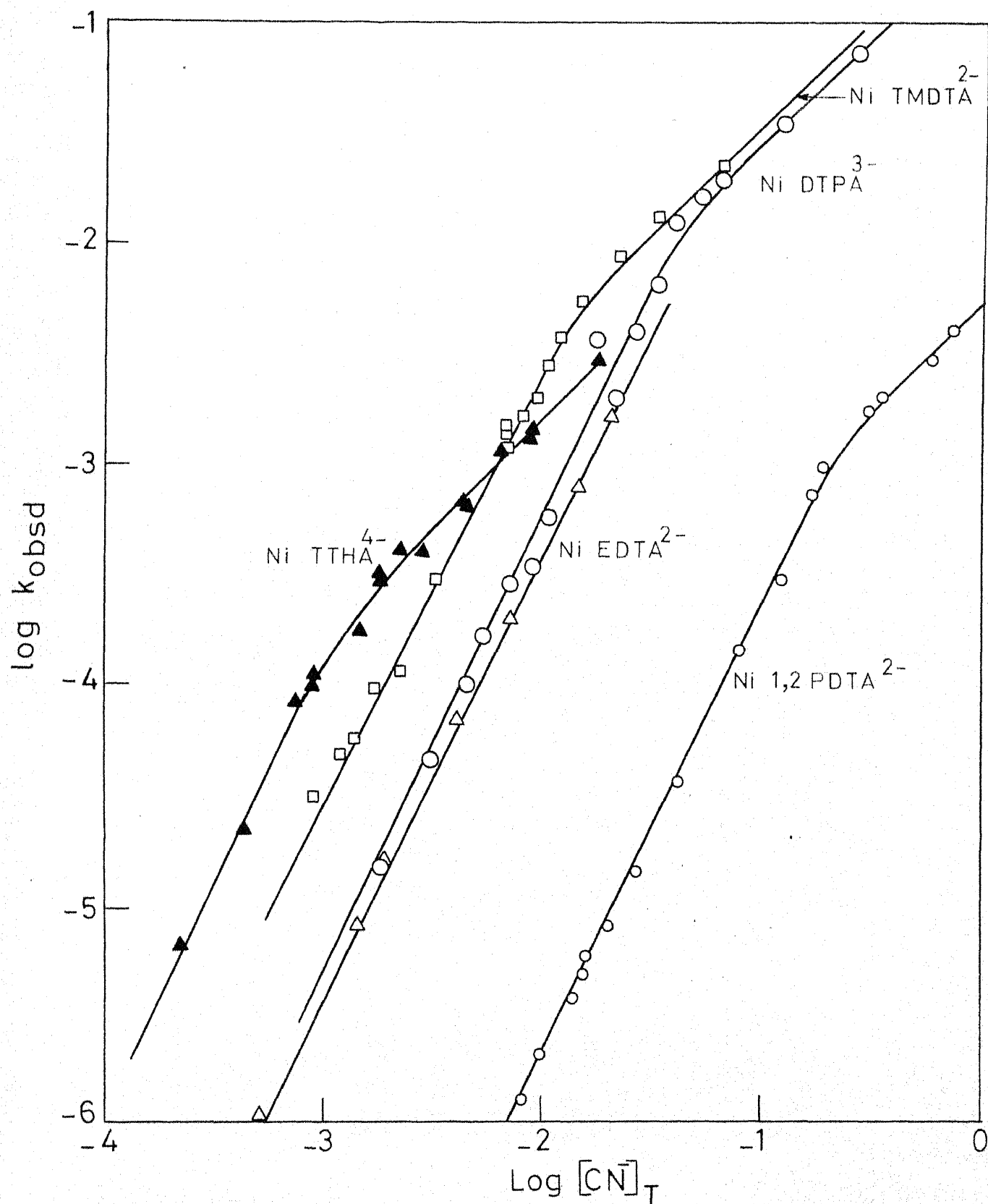


Fig. II.11 Cyanide dependence of the observed Forward Rate constants in NiTMDTA^{2-} , Ni-1,2-PDTA^{2-} , NiDTPA^{3-} , NiTTHA^{4-} and NiEDTA^{2-} Systems at $25 \pm 0.1^\circ\text{C}$; $\text{pH} = 11.0$; and $\mu = 0.1 \text{ M}$. The solid line is calculated from k_3 and K_2k_3

A simple explanation of variable order in cyanide ion concentration changing from 3 to 1, is that a total of three cyanide ions are needed in the rate determining step and the observed order depends upon how many of the three cyanides are already complexed to the nickel-aminocarboxylate. The general rate expression for forward reaction is given in Equation (6):

$$\begin{aligned} d[\text{Ni}(\text{CN})_4^{2-}] / dt &= k_{\text{obsd}} [\text{NiL}(\text{CN})_x^{2-n-x}] \\ &= k_f [\text{NiL}(\text{CN})_x^{2-n-x}] [\text{CN}^-]^{3-x} \end{aligned} \quad \text{..(6)}$$

The slopes of Figure II.11 are found to be equal to 3-x, where x varies from 1 to 2 in the present case as cyanide concentration increases from low to high (Figure II.11). Thus monocyano and bicyano complexes are formed in each case during the course of reactions. As will be demonstrated later, the stability constant of these intermediates as defined in Equations (7) and (8) can be determined from kinetic data of the forward and reverse rate studies:

$$K_1 = \frac{[\text{NiL}(\text{CN})^{1-n}]}{[\text{NiL}^{2-n}] [\text{CN}^-]} \quad \text{..(7)}$$

$$\begin{aligned} K_2 &= \frac{[\text{NiL}(\text{CN})_2^{n-}]}{[\text{NiL}(\text{CN})^{1-n}] [\text{CN}^-]} \\ &= \frac{[\text{NiL}(\text{CN})_2^{n-}]}{K_1 [\text{NiL}^{2-n}] [\text{CN}^-]^2} \end{aligned} \quad \text{..(8)}$$

Kinetics of Reverse Reactions

At high pH (~11.0) there is no noticeable dissociation of $\text{Ni}(\text{CN})_4^{2-}$ even on long standing. Using very dilute solutions

of $\text{Ni}(\text{CN})_4^{2-}$ ($\sim 10^{-5}$ M) and high concentration of L^{n-} (amino-carboxylates) it becomes possible to force reaction (1) in the reverse direction. As in case of forward rate an immediate decrease in absorbance of the reaction mixture was noticed following mixing of the reactants. This is again due to the formation of an intermediate $\text{NiL}(\text{CN})_3$ to be consistent with the forward rate data as well. A rate expression consistent with observations is given in Equation (9):

$$-d[\text{Ni}(\text{CN})_4^{2-}]/dt = k_r [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}] / [\text{CN}^-] \quad \dots(9)$$

The integrated form of Equation (9) is given in Equation (10)

$$(A_i - A_t) + A_i \ln A_t / A_i = - \frac{\epsilon \cdot l}{4} \cdot k'_{\text{obsd}} t \quad \dots(10)$$

where A_i and A_t are absorbances at time $t = 0$ and $t = t$, and ϵ is molar absorptivity of $\text{Ni}(\text{CN})_4^{2-}$ at the wavelength at which the reaction is monitored. Plots of left hand side of Equation (10) versus time give straight lines and the slopes of these lines give k'_{obsd} (Figure II.12) where $k'_{\text{obsd}} = k_r [\text{L}^{n-}]$, k_r being the reverse rate constant. The plots of $\log k'_{\text{obsd}}$ versus \log (aminocarboxylate) give straight lines which again confirms that the reverse reactions are first order with respect to aminocarboxylate concentration (Table II.4 and Figure II.13).

Finally, a mechanism which is in line with the observation on forward and reverse rates can be written down (Equations 11 to 14). A more rigorous justification for this will be given later (see discussion part):

Table II.4. Rate constants for reverse reaction at temp = 25°C

TMDTA⁴⁻: pH = 11.0 ± 0.2; μ = 0.5 M (NaClO₄), $[\text{Ni}(\text{CN})_4^{2-}] = 4.44 \times 10^{-5} \text{ M}$

$10^3 [\text{TMDTA}^{4-}] \text{ M}$	$10^{10} k'_{\text{obsd}}, \text{ MS}^{-1}$	$10^7 k_r, \text{ S}^{-1}$
0.625	1.40	2.20
1.25	2.50	2.00
2.50	3.98	1.60
5.00	10.00	2.02
<hr/>		
av. = (1.96 ± 0.17)		

pH = 11.0 ± 0.2; μ = 0.5 M (KNO₃); $[\text{Ni}(\text{CN})_4^{2-}] = 5.00 \times 10^{-5} \text{ M}$.

0.625	4.13	6.60
0.833	5.45	6.54
2.50	22.00	8.80
5.00	37.00	7.50
<hr/>		
av. = (7.36 ± 0.53)		

1,2-PDTA⁴⁻: pH = 11.0 ± 0.2; μ = 0.5 M (NaClO₄); $[\text{Ni}(\text{CN})_4^{2-}] = 6.38 \times 10^{-5} \text{ M}$.

$10^2 [1,2\text{-PDTA}^{4-}] \text{ M}$	$10^{11} k'_{\text{obsd}}, \text{ MS}^{-1}$	$10^9 k_r, \text{ S}^{-1}$
1.50	3.97	2.64
2.00	6.64, 6.60	3.31, 3.30
2.50	7.37, 7.39	2.95, 2.96
<hr/>		
av. = (3.03 ± 0.20)		

...contd.

Table II.4 (contd.)

DTPA⁶⁻: pH = 11.0 ± 0.2; $\mu = 0.5$ M(NaClO₄); $[\text{Ni}(\text{CN})_4^{2-}] = 6.38 \times 10^{-5}$ M.

$10^3 [\text{DTPA}^{5-}], \text{M}$	$10^{10} k'_{\text{obsd}}$	$10^8 k_r, \text{s}^{-1}$
1.25	0.68	5.5
2.50	1.36, 1.37	5.4, 5.5
6.25	2.57, 2.56	4.10, 4.10
<hr/>		
av. = (5.00 ± 0.45)		

TTHA⁶⁻: pH = 11.0 ± 0.2; $\mu = 0.5$ M(NaClO₄); $[\text{Ni}(\text{CN})_4^{2-}] = 6.0 \times 10^{-5}$ M.

$10^3 [\text{TTHA}^{6-}], \text{M}$	$10^{10} k'_{\text{obsd}}$	$10^7 k_r, \text{s}^{-1}$
1.56	6.00	4.00
2.09	7.01	3.30
3.13	10.00	3.10
4.18	12.20	2.90
4.18	13.00	3.00
6.25	16.70	2.67
12.50	30.00	2.60
<hr/>		
av. = (3.08 ± 0.17) × 10 ⁻⁷ *		

A better value ($= 2.20 \times 10^7 \text{ s}^{-1}$) comes from graphical analysis.

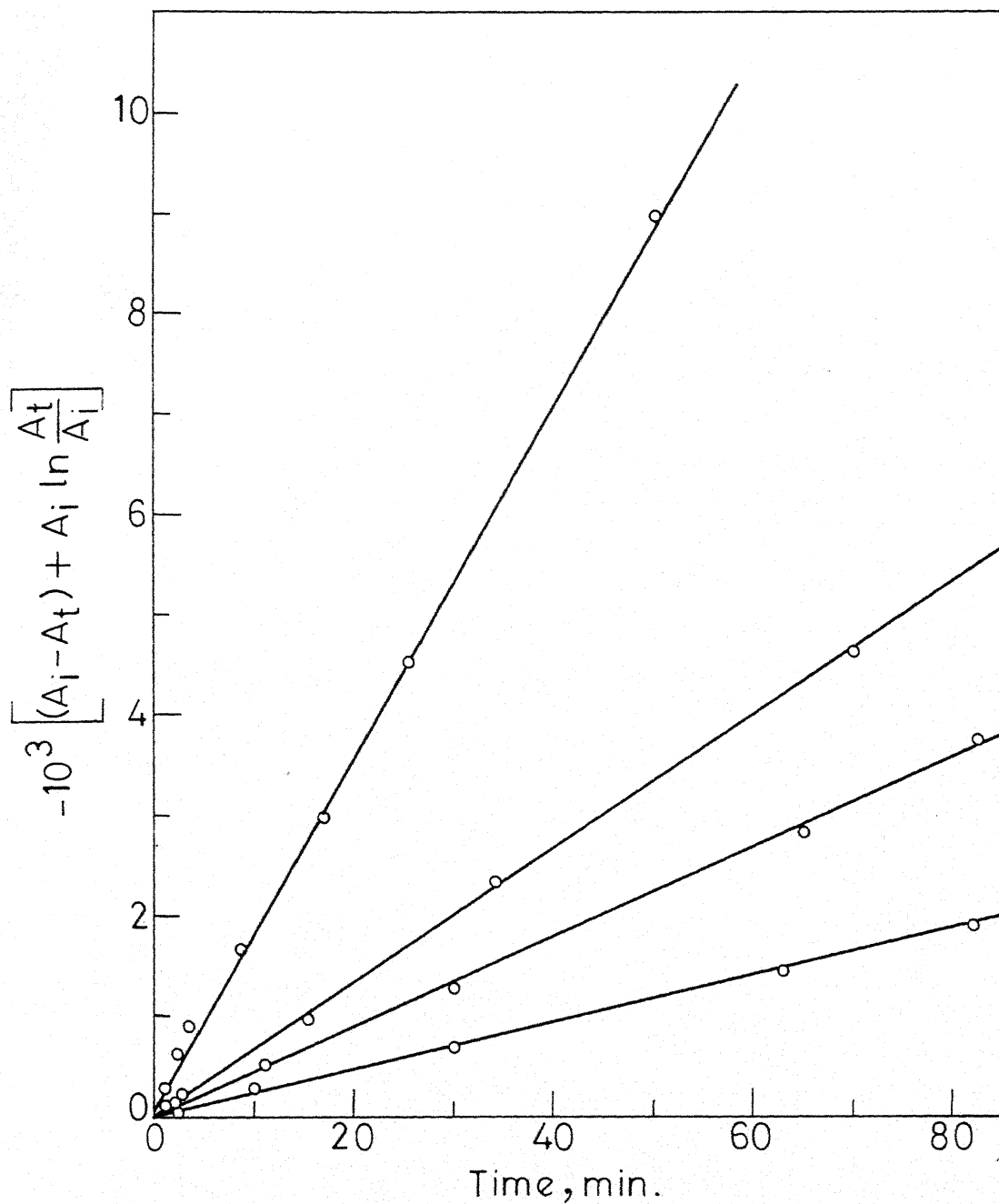


FIG. 11.12 Inverse First Order Plots for Reaction of $\text{K}_2\text{Cr}_2\text{O}_7$ with TMMA at temp = 25°C : $\text{pH} = 11.0$ and $\mu = 0.5 \text{ M}$.

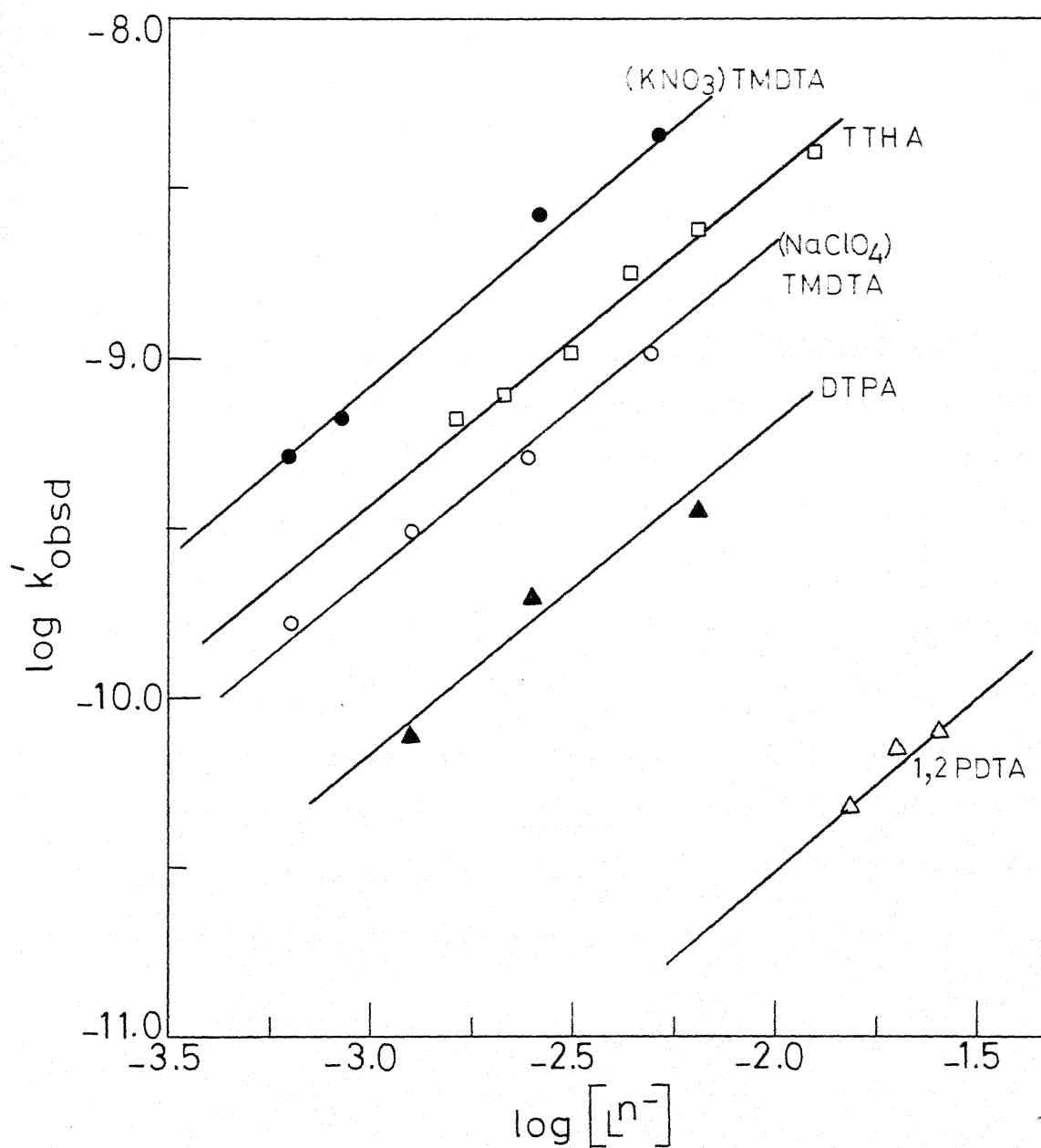
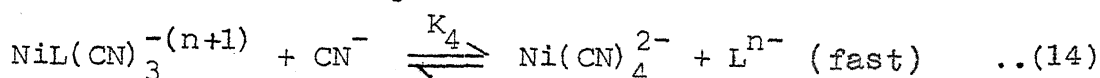
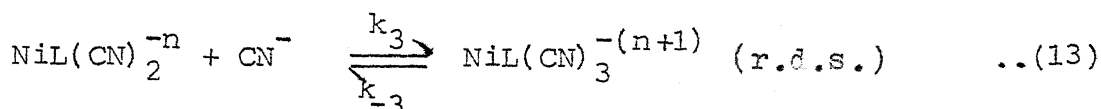
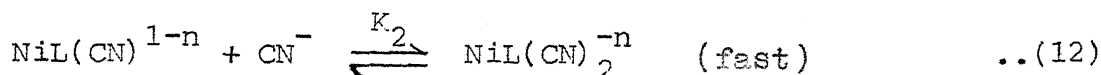
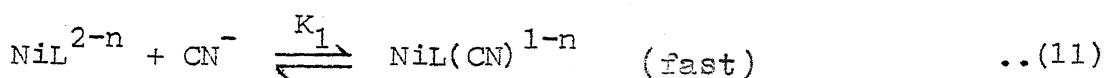


Fig. 11.13 Ligand Dependence of Observed Rate Constants for the Reaction of $\text{Ni}(\text{CN})_4^{2-}$ with Aminocarboxylates



Dependence of Forward and Reverse Rates on Temperature

Both forward and reverse reactions were carried out at different temperatures in the range 25-50°C. All reactions were found to follow the Arrhenius Equation (15) over the entire temperature range.

$$\ln k = -E_a/RT + \ln A \quad \dots (15)$$

The activation energies and enthalpies of activation have been calculated from plots of $\ln k$ versus $1/T$ (Figure II.14 and II.15) while the entropies of activation (ΔS^\ddagger) and probability factors pZ were calculated from Equation (16):

$$k_2 = \frac{kT}{h} \cdot e^{-\Delta G^\ddagger/RT} = \frac{kT}{h} \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT} = pZ e^{-\Delta H^\ddagger/RT} \quad \dots (16)$$

The activation parameters for all forward reactions were determined at cyanide concentrations where the order dependence is 2 and are given in Table II.5. For reverse reactions these are compiled in Table II.6. The values of activation parameters have later been used to elucidate the proposed reaction mechanism.

Table II.5. Temperature effect on forward reaction of
 $\text{NiL}^{2-} - (\text{CN}^-)$ reaction systems

Temp. °C	$[\text{CN}^-]_T$	$k_{\text{obsd}}, \text{ s}^{-1}$	Kinetic parameters
(i) <u>NiTMDDTA-CN⁻</u>			
$[\text{NiTMDDTA}^{2-}] = 5.86 \times 10^{-5} \text{ M}; \text{ pH} = 11.0 \pm 0.2; \mu = 0.1 \text{ M}(\text{NaClO}_4)$			
25 ± 0.1	1.20×10^{-3}	4.00×10^{-5}	E_a kcal 5.93
	5.00×10^{-3}	7.76×10^{-4}	pZ cm ⁻¹ 2.43×10^5
30 ± 0.1	1.20×10^{-3}	4.48×10^{-5}	ΔH^\ddagger kcal 5.34
	5.00×10^{-3}	9.06×10^{-4}	ΔS^\ddagger e.u. -33.78
35 ± 0.1	1.20×10^{-3}	5.28×10^{-5}	
	5.00×10^{-3}	1.09×10^{-3}	
40 ± 0.1	1.20×10^{-3}	6.23×10^{-5}	
	5.00×10^{-3}	1.29×10^{-3}	
45 ± 0.1	1.20×10^{-3}	8.94×10^{-5}	
	5.00×10^{-3}	1.63×10^{-3}	
(ii) <u>Ni 1,2-PDDTA-CN⁻</u>			
$[\text{Ni 1,2-PDDTA}^{2-}] = 9.05 \times 10^{-5} \text{ M}; \text{ pH} = 11.0 \pm 0.2; \mu = 0.1 \text{ M}(\text{NaClO}_4)$			
30 ± 0.1	1.24×10^{-1}	9.84×10^{-4}	E_a kcal 4.41
	2.48×10^{-1}	4.10×10^{-3}	pZ cm ⁻¹ 37.29
35 ± 0.1	1.24×10^{-1}	1.45×10^{-3}	ΔH^\ddagger kcal 3.82
	2.48×10^{-1}	4.99×10^{-3}	ΔS^\ddagger e.u. -51.19
45 ± 0.1	1.24×10^{-1}	2.03×10^{-3}	
	2.48×10^{-1}	8.63×10^{-3}	
50 ± 0.1	1.24×10^{-1}	2.97×10^{-3}	
	2.48×10^{-1}	-	...contd.

Table II.5 (contd.)

(iii) NiDTPA-CN⁻

$[\text{NiDTPA}^{3-}] = 4.41 \times 10^{-5} \text{ M}; \text{ pH} = 11.0 \pm 0.2; \mu = 0.1 \text{ M}(\text{NaClO}_4)$				
25 \pm 0.1	5.68×10^{-3}	2.77×10^{-4}	E_a kcal	3.74
	8.75×10^{-3}	3.94×10^{-4}	pZ cm ⁻¹	1.06×10^3
40 \pm 0.1	5.68×10^{-3}	3.45×10^{-4}	ΔH^\ddagger kcal	3.15
	8.75×10^{-3}	5.10×10^{-4}	ΔS^\ddagger e.u.	-44.5
50 \pm 0.1	5.68×10^{-3}	4.47×10^{-4}		
	8.75×10^{-3}	6.58×10^{-4}		

(iv) NiTTHA-CN⁻

$[\text{NiTTHA}^{4-}] = 7.06 \times 10^{-5} \text{ M}; \text{ pH} = 11.0 \pm 0.2; \mu = 0.1 \text{ M}(\text{NaClO}_4)$				
25 \pm 0.1	1.80×10^{-3}	2.60×10^{-4}	E_a kcal	12.30*
30 \pm 0.1	1.80×10^{-3}	3.70×10^{-4}	pZ cm ⁻¹	6.00×10^7
35 \pm 0.1	1.80×10^{-3}	4.62×10^{-4}	ΔH^\ddagger kcal	11.71
40 \pm 0.1	1.80×10^{-3}	7.13×10^{-4}	ΔS^\ddagger e.u.	-22.88

This value is high compared to E_a of similar reactions but with only four available values it is not possible to provide an explanation.

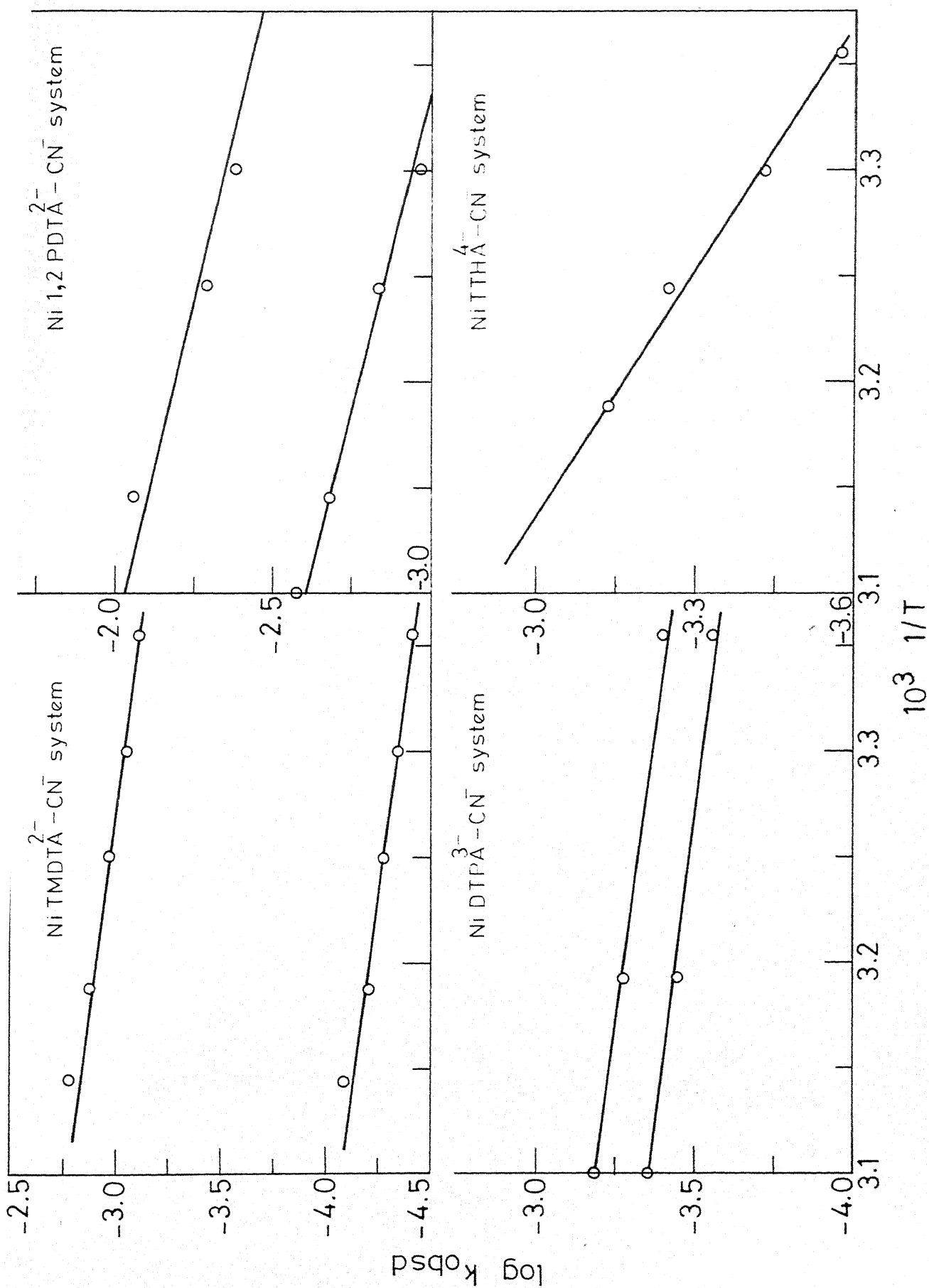


Fig. 11.14 Effect of Temperature on the Forward Reaction

Table II.6. Temperature effect on reverse reaction of
 $\text{NiL}^{2-n} - \text{CN}^-$ reaction system

Temp. °C	[L] _T , M	k' _{obsd} , MS ⁻¹	Kinetic parameter	
(i) <u>Ni(CN)₄²⁻-TMDTA</u>				
[Ni(CN) ₄ ²⁻] = 4.35×10 ⁻⁵ M; pH = 11.0±0.2; μ = 0.5 M (NaClO ₄)				
25 ± 0.1	1.25 × 10 ⁻³	2.76 × 10 ⁻¹⁰	E _a kcal	20.80
35 ± 0.1	1.25 × 10 ⁻³	5.57 × 10 ⁻¹⁰	pZ cm ⁻¹	1.47×10 ⁸
40 ± 0.1	1.25 × 10 ⁻³	7.64 × 10 ⁻¹⁰	ΔH [‡] kcal	20.21
45 ± 0.1	1.25 × 10 ⁻³	1.21 × 10 ⁻⁹	ΔS [‡] e.u.	-20.10
50 ± 0.1	1.25 × 10 ⁻³	2.47 × 10 ⁻⁹		
(ii) <u>Ni(CN)₄²⁻- 1,2-PDTA</u>				
[Ni(CN) ₄ ²⁻] = 6.38×10 ⁻⁵ M; pH = 11.0±0.2; μ = 0.5 M (NaClO ₄)				
25 ± 0.1	2.00 × 10 ⁻²	6.64 × 10 ⁻¹¹	E _a kcal	27.39
	2.50 × 10 ⁻²	7.37 × 10 ⁻¹¹	pZ cm ⁻¹	1.58×10 ¹¹
40 ± 0.1	2.00 × 10 ⁻²	5.99 × 10 ⁻¹⁰	ΔH [‡] kcal	26.8
	2.50 × 10 ⁻²	7.27 × 10 ⁻¹⁰	ΔS [‡] e.u.	-7.36
50 ± 0.1	2.00 × 10 ⁻²	1.92 × 10 ⁻⁹		
	2.50 × 10 ⁻²	2.25 × 10 ⁻⁹		
60 ± 0.1	2.00 × 10 ⁻²	4.90 × 10 ⁻⁹		
	2.50 × 10 ⁻²	7.28 × 10 ⁻⁹		
(iii) <u>Ni(CN)₄²⁻ - DTPA</u>				
[Ni(CN) ₄ ²⁻] = 6.25×10 ⁻⁵ M; pH = 11.0±0.2; μ = 0.5 M (NaClO ₄)				
25 ± 0.1	2.50 × 10 ⁻³	1.36 × 10 ⁻¹⁰	E _a kcal	30.03
	6.25 × 10 ⁻³	2.57 × 10 ⁻¹⁰	pZ cm ⁻¹	1.95×10 ¹⁴

...contd.

Table II.6 (contd.)

40 \pm 0.1	2.50 $\times 10^{-3}$	1.70 $\times 10^{-9}$	ΔH° kcal	29.45
	6.25 $\times 10^{-3}$	1.88 $\times 10^{-9}$	ΔS° e.u.	6.81
50 \pm 0.1	2.50 $\times 10^{-3}$	3.65 $\times 10^{-9}$		
	6.25 $\times 10^{-3}$	1.49 $\times 10^{-8}$		

(iv) $\text{Ni}(\text{CN})_4^{2-}$ - TTHA
$$[\text{Ni}(\text{CN})_4^{2-}] = 4.00 \times 10^{-5} \text{ M}; \text{pH} = 11.0 \pm 0.2; \mu = 0.5 \text{ M (NaClO}_4\text{)}$$

25 \pm 0.1	4.18 $\times 10^{-3}$	1.33 $\times 10^{-9}$	E_a kcal	17.06
30 \pm 0.1	4.18 $\times 10^{-3}$	1.88 $\times 10^{-9}$	pZ cm^{-1}	4.09 $\times 10^5$
35 \pm 0.1	4.18 $\times 10^{-3}$	2.58 $\times 10^{-9}$	ΔH° kcal	16.47
40 \pm 0.1	4.18 $\times 10^{-3}$	4.21 $\times 10^{-9}$	ΔS° e.u.	-32.75
50 \pm 0.1	4.18 $\times 10^{-3}$	7.80 $\times 10^{-9}$		

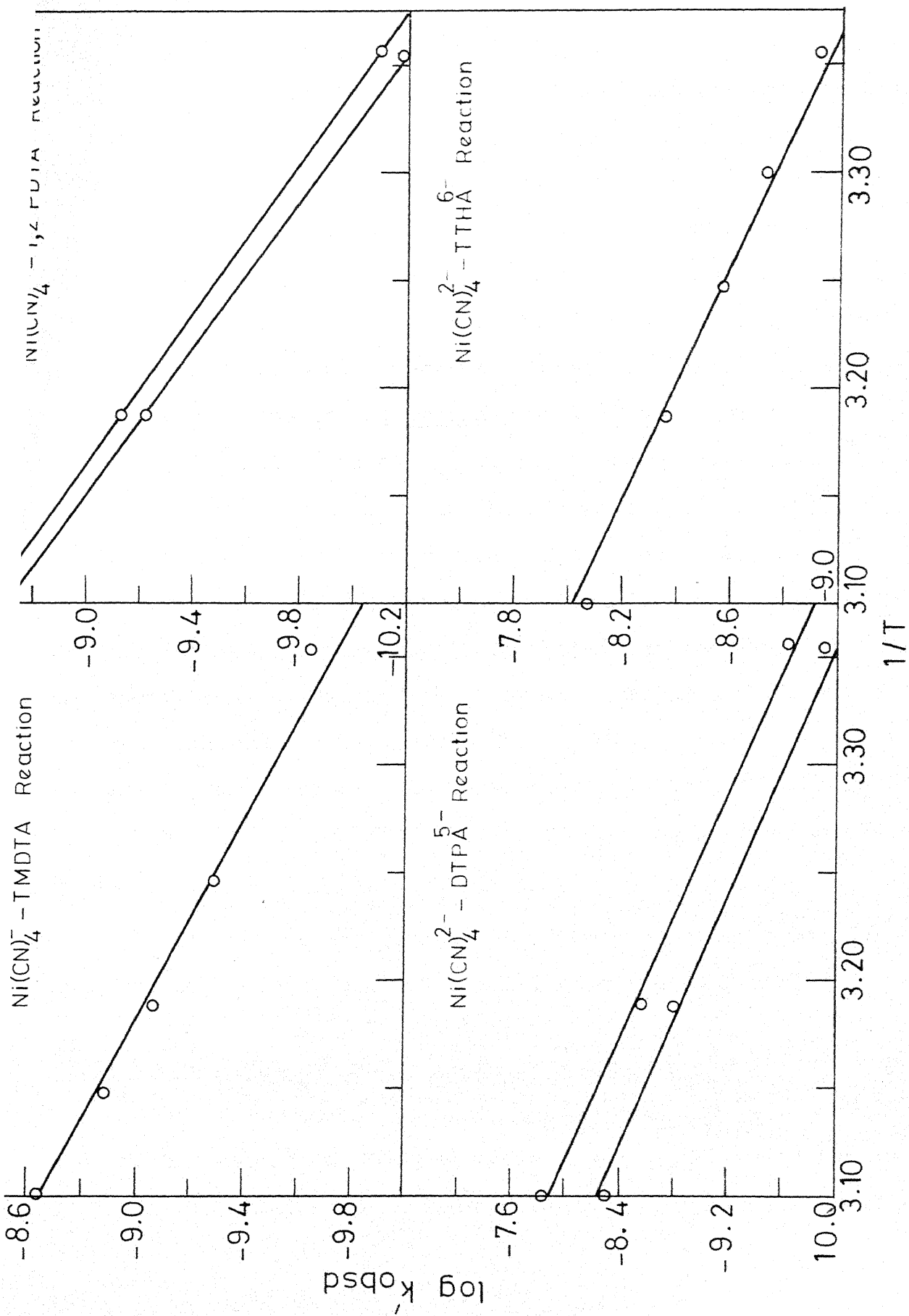


FIG. 11.15 Effect of Temperature on the Reverse Reaction

Dependence of the Forward Rate on pH

The rate constants for reaction (1) were measured in the pH range 7.0-11.5 at constant $[\text{CN}^-]_{\text{T}}$, where $[\text{CN}^-]_{\text{T}} = [\text{CN}^-] + [\text{HCN}]$. The observed forward rate constants (k_{obsd}) are given in Table II.7. It is observed that rate constants from pH 10.0-11.5 are constant but below pH 9.0 the rate decreases (Figure II.16). A slope of 2 would be expected in the pH region close to 8 if HCN was not a reactant. However, a slope of only 1 is observed in the $\log k_f$ versus $-\log [\text{H}^+]$ plots (where $(k_f = k_{\text{obsd}} / [\text{CN}^-]_{\text{T}}^2)$) for all reactions. Stara and Kopanica⁸ reported a slope equal to 2 in the NiTTHA reaction, which, of course, could not be reproduced when a check was made on their data. The above observation is consistent with one molecule of HCN and one molecule of CN^- being the reactants in this pH range. One interesting observation below pH 7.5 is that the rate constant deviates from the expected values. This appears to be due to fall in concentration of $\text{NiL}(\text{CN})$ below this pH as a result of depletion of CN^- following its conversion to HCN.

A rate expression consistent with these observation for the entire pH range from 7.0 to 11.5 is given in Equation (17):

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = \{K_2 k_3 [\text{CN}^-]^2 + K_2 k'_3 [\text{CN}^-][\text{HCN}]\} [\text{NiL}(\text{CN})] \quad \dots (17)$$

when k'_3 corresponds to HCN reaction. The solid line in Figure II.16 is the calculated line from $-\log [\text{H}^+]$, pK_a of HCN and rate

Table II.7. Effect of pH on tetracyanonickelate formation

$-\log [H^+]$	k_{obsd}, s^{-1}	$k_f = \frac{k_{\text{obsd}}}{[CN^-]_T^2}, M^{-2} s^{-1}$
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(i) Ni(TMDTA²⁻) - CN⁻ reaction system

$[NiTMDTA^{2-}] = 4.31 \times 10^{-5} M$; $[CN^-]_T = 6.40 \times 10^{-3} M$; $\mu = 0.1 M (NaClO_4)$;
Temp. = 25°C

6.80	1.00×10^{-5}	0.24
7.40	4.14×10^{-5}	1.00
7.90	8.60×10^{-5}	2.10
8.40	1.70×10^{-4}	4.15
8.65	3.07×10^{-4}	7.47
9.40	8.96×10^{-4}	21.88
9.90	9.31×10^{-4}	22.73
10.40	1.01×10^{-43}	24.86
10.90	1.01×10^{-43}	24.66
11.40	0.988×10^{-43}	23.88

(ii) Ni(1,2-PDTA²⁻) - CN⁻ reaction system

$[Ni\ 1,2-PDTA] = 9.7 \times 10^{-5}$; $[CN^-]_T = 2.50 \times 10^{-2} M$; $\mu = 0.1 M (NaClO_4)$;
Temp = 40°C.

8.25	8.31×10^{-6}	1.33×10^{-2}
8.55	1.57×10^{-5}	2.51×10^{-2}
9.00	3.73×10^{-5}	5.96×10^{-2}
9.10	4.96×10^{-5}	7.94×10^{-2}
9.50	7.63×10^{-5}	1.22×10^{-1}
10.10	7.88×10^{-5}	1.26×10^{-1}
10.80	7.81×10^{-5}	1.25×10^{-1}

...contd.

Table II.7 (contd.)

(iii) NiDTPA^{3-} - CN^- reaction system

$$[\text{NiDTPA}^{3-}] = 4.41 \times 10^{-5} \text{ M}; [\text{CN}^-]_{\text{T}} = 1.07 \times 10^{-2} \text{ M}; \mu = 0.1 \text{ M (NaClO}_4\text{)};$$

Temp = 40°C.

7.1	1.89×10^{-4}	1.65
7.3	2.64×10^{-4}	3.34
7.8	9.52×10^{-4}	8.32
8.5	2.08×10^{-3}	8.18
9.0	5.00×10^{-3}	43.65
9.4	5.74×10^{-3}	50.11
9.8	6.00×10^{-3}	52.48
10.4	5.06×10^{-3}	51.29
11.15	5.06×10^{-3}	51.29

(iv) NiTTHA^{4-} - CN^- reaction system

$$[\text{NiTTHA}^{4-}] = 5.80 \times 10^{-5} \text{ M}; [\text{CN}^-]_{\text{T}} = 9.00 \times 10^{-4} \text{ M}; \mu = 0.1 \text{ M (NaClO}_4\text{)};$$

Temp = 25°C.

7.40	4.79×10^{-7}	0.59
7.90	1.12×10^{-6}	2.34
8.40	3.83×10^{-6}	4.73
8.70	5.75×10^{-6}	7.10
8.90	1.00×10^{-5}	12.42
9.10	1.73×10^{-5}	21.30
9.60	4.73×10^{-5}	58.43
9.90	9.35×10^{-5}	115.43
10.10	9.50×10^{-5}	117.28
10.40	9.80×10^{-5}	120.99
10.90	1.00×10^{-4}	123.46
11.10	1.00×10^{-4}	123.46

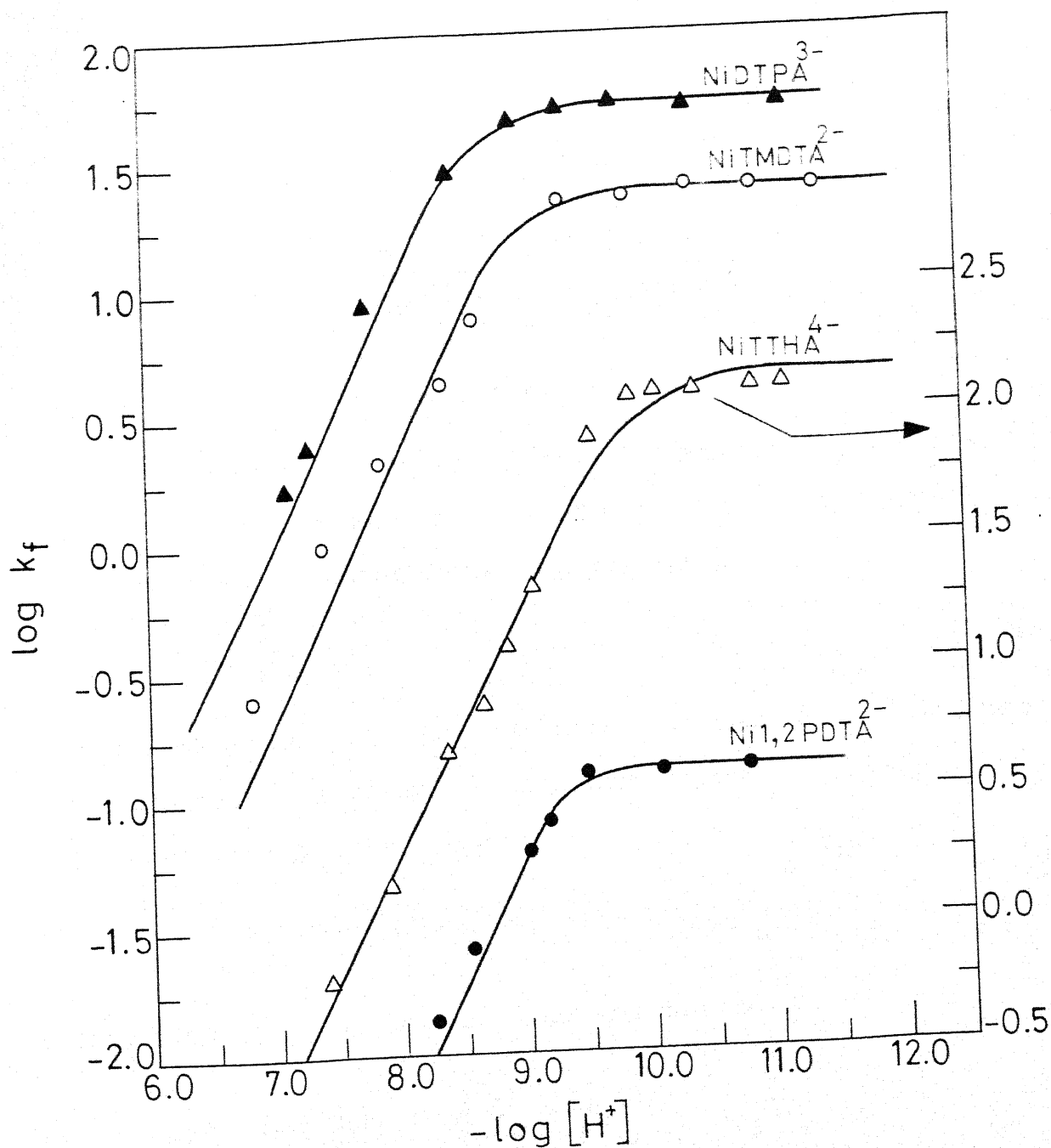


Fig. 11.16 Effect of pH on the Forward Reaction of $NiL^{2-}-CN^-$ Reaction System. The solid curves are calculated from Resolved rate Constants k_2k_3 and $k_2k'_3$

constants K_2k_3 and $K_2k'_3$ whose values have been resolved as under:

$$\begin{aligned}
 k_{\text{obsd}} &= k_f [\text{CN}^-]_T^2 = K_2k_3 [\text{CN}^-]^2 + K_2k'_3 [\text{CN}^-] [\text{HCN}] \\
 k_f \{ [\text{CN}^-] + [\text{HCN}] \}^2 &= K_2k_3 [\text{CN}^-]^2 + K_2k'_3 [\text{CN}^-] [\text{HCN}] \\
 k_f &= \frac{K_2k_3 [\text{CN}^-]^2 + K_2k'_3 [\text{CN}^-]^2 K_H [\text{H}^+]}{[\text{CN}^-]^2 \{ 1 + 2 K_H [\text{H}^+] + K_H^2 [\text{H}^+]^2 \}} \quad \dots (18)
 \end{aligned}$$

where K_H is protonation constant of HCN.

At higher pH, the second term in numerator and the second and third term in denominator of Equation (18) can be neglected in comparison to other terms, and one gets

$$k_f = K_2k_3 \quad \dots (19)$$

On the other hand at lower pH, the first term in the numerator and the first and second term in denominator can be neglected in comparison to other terms and

$$k_f = \frac{K_2k'_3}{K_H [\text{H}^+]} \quad \dots (20)$$

Combining Equations (19) and (20) one can get

$$k_f = K_2k_3 + \frac{K_2k'_3}{K_H} \cdot \frac{1}{[\text{H}^+]} \quad \dots (21)$$

The data for all four ligands are plotted in Figure II.17 and are also presented in Table II.8. Calculated value of K_2k_3 and $K_2k'_3$ for each ligand making use of Equation 21 have also been

Table II.8. Resolution of rate constants into rate constants due to CN^- and HCN

$-\log [\text{H}^+]$	$[\text{H}^+]$	$1/[\text{H}^+]$	$k_f, \text{M}^{-2}\text{s}^{-1}$
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1. $\text{NiTMDTA}^{2-}-\text{CN}^-$ Reaction System

$[\text{NiL}]_i = 4.31 \times 10^{-5} \text{ M}; [\text{CN}]_T = 6.40 \times 10^{-3}; \mu = 0.1 \text{ M (NaClO}_4\text{)};$
 $t = 25^\circ\text{C}$

7.40	3.98×10^{-8}	0.25×10^8	0.83
7.90	1.26×10^{-8}	0.79×10^8	2.10
8.40	3.98×10^{-9}	2.51×10^8	4.15
8.65	1.99×10^{-9}	5.01×10^8	7.47

Calcd $K_2k_3 = 2.85 \times 10^1 \text{ M}^{-2}\text{s}^{-1}; K_2k'_3 = 14.3 \text{ M}^{-2}\text{s}^{-1}$

2. $\text{Ni 1,2-PDTA}^{2-}-\text{CN}^-$ Reaction System

$[\text{NiL}]_i = 9.76 \times 10^{-5} \text{ M}; [\text{CN}]_T = 2.50 \times 10^{-2} \text{ M}; \mu = 0.1 \text{ M (NaClO}_4\text{)};$
 $t = 40^\circ\text{C}$

8.25	5.62×10^{-9}	1.78×10^8	1.30×10^{-2}
8.55	2.82×10^{-9}	3.54×10^8	3.09×10^{-2}
9.00	1.00×10^{-9}	10.00×10^8	5.96×10^{-2}
9.10	7.07×10^{-10}	14.13×10^8	7.90×10^{-2}

Calcd $K_2k_3 = 1.20 \times 10^{-2} \text{ M}^{-2}\text{s}^{-1}; K_2k'_3 = 5.5 \times 10^{-2} \text{ M}^{-2}\text{s}^{-1}$

3. $\text{NiDTPA}^{3-}-\text{CN}^-$ Reaction System

$[\text{NiL}]_i = 4.41 \times 10^{-5} \text{ M}; [\text{CN}]_T = 1.07 \times 10^{-2} \text{ M}; \mu = 0.1 \text{ M (NaClO}_4\text{)};$
 $t = 40^\circ\text{C}$

7.1	7.94×10^{-8}	0.13×10^8	1.66
7.3	5.01×10^{-8}	0.20×10^8	2.34
7.8	1.58×10^{-8}	0.63×10^8	8.31
8.5	3.16×10^{-9}	3.16×10^8	28.18

Calcd $K_2k_3 = 51.57 \text{ M}^{-2}\text{s}^{-1}; K_2k'_3 = 13.30 \text{ M}^{-2}\text{s}^{-1}.$...contd.

Table II.8 (contd.)

4. NiTTHA^{4-} - CN^- Reaction System

$$[\text{NiL}]_i = 5.80 \times 10^{-5} \text{ M} ; [\text{CN}^-]_T = 9.00 \times 10^{-4} ; \mu = 0.1 \text{ M} (\text{NaClO}_4)$$

t = 25°C

7.40	3.98×10^{-8}	0.25×10^8	0.59
7.90	1.26×10^{-8}	0.79×10^8	1.38
8.40	2.98×10^{-9}	2.51×10^8	4.73
8.70	1.99×10^{-9}	5.01×10^8	7.10
8.90	1.26×10^{-9}	7.94×10^8	12.42
9.10	7.94×10^{-10}	12.60×10^8	21.32

$$\text{Calcd } K_2 k_3 = 120 \text{ M}^{-2} \text{ s}^{-1} ; K_2 k'_3 = 16.7 \text{ M}^{-2} \text{ s}^{-1}$$

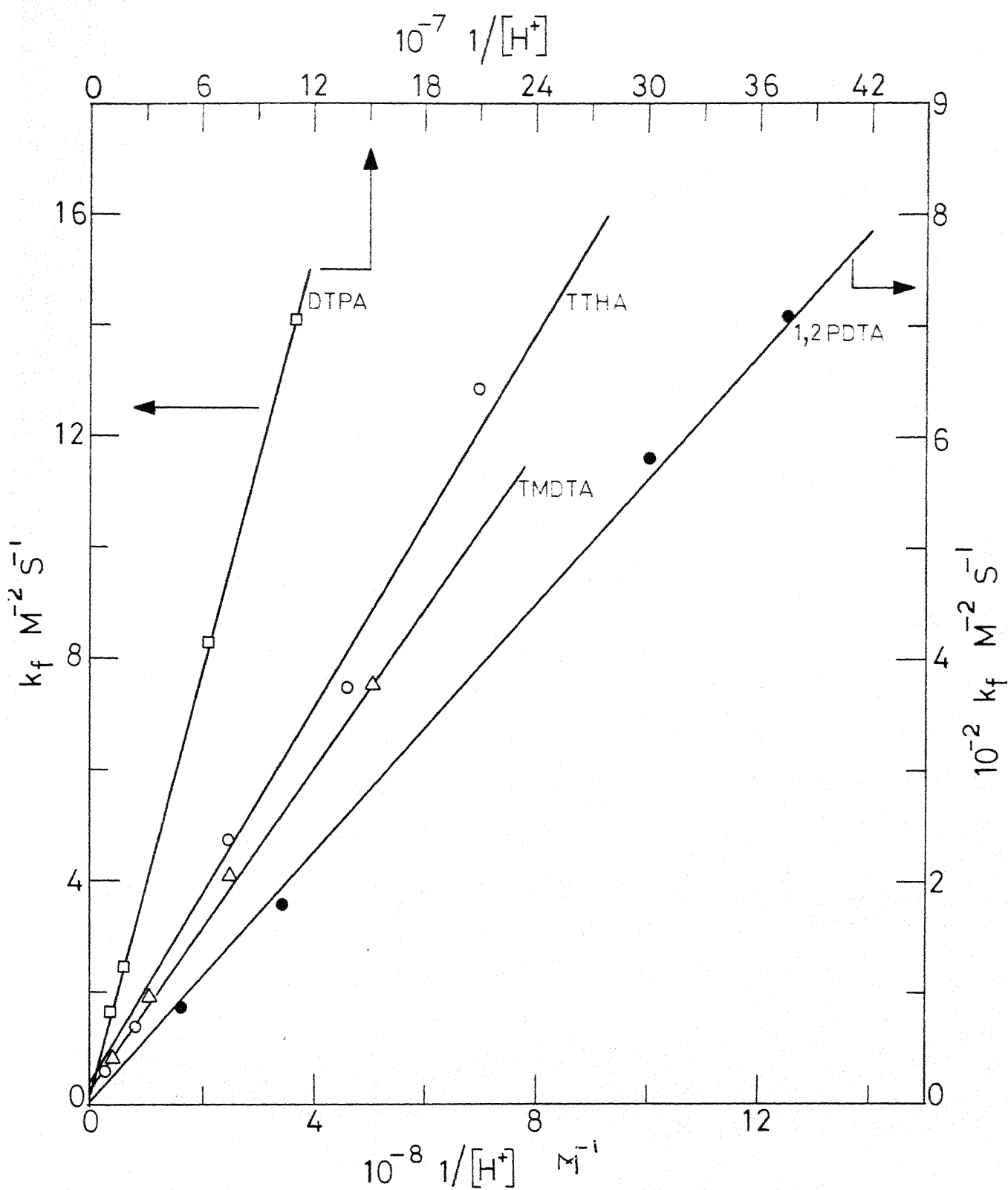


Fig. 11.17 Resolution of Forward Rate Constants into K_2k_3 and K_2k_3'

included in the Table II.17.

pH Dependence of Reverse Reaction

The reverse reactions for all the four ligands have been studied in a wide range of pH. It is found that, in general, the rate of reaction decreases as pH decreases upto pK_a of a particular ligand. This behaviour is attributed to the formation of one or more protonated but less reactive forms HL , H_2L , H_3L --- etc. It is again possible to deduce the hydrogen ion dependence of reverse reaction by the expression (22):

$$k_r [L]_T = k_L [L^{n-}] + k_{HL} [HL^{-(n-1)}] + k_{H_2L} [H_2L^{-(n-2)}] + k_{H_3L} [H_3L^{-(n-3)}] \dots (22)$$

$$\text{where } [L]_T = [L^{n-}] + [HL^{-(n-1)}] + [H_2L^{-(n-2)}] + \dots$$

It would be convenient to illustrate the procedure with reference to TTHA as an example. A closer look at the species distribution (Figure II.10) for the specific case of TTHA reveals that the concentration of the protonated species involving more than two protons are not more than 1% and can be ignored. *Since their contribution to the rate is expected to be insignificant* Equation (22), therefore, takes the form given in Equation (23):

$$k_r \{ [L^{n-}] + [HL^{-(n-1)}] + [H_2L^{-(n-2)}] \} = k_L [L^{n-}] + k_{HL} [HL^{-(n-1)}] + k_{H_2L} [H_2L^{-(n-2)}] \dots (23)$$

where k_L , k_{HL} and k_{H_2L} are rate constants due to unprotonated, monoprotonate and diprotonated forms respectively of TTHA.

Expression (23) is not a simple expression. The plot of $\log k'_{\text{obsd}}$ versus pH gives a curve shown in Figure II.18 and the related data are presented in Table II.9. The solid curve shown in Figure II.18 has been calculated on the basis of values of k_L , k_{HL} , k_{H_2L} and pK_a 's of TTHA. From these values one can easily see that in case of TTHA reaction with $Ni(CN)_4^{2-}$, $TTHA^{6-}$ and H_2TTHA^{4-} are more reactive than $HTTHA^{5-}$. This type of observations were also reported by Carr and Danielson⁵³ for 1,2-PDTA reaction with $NiEDTA^{2-}$ and by Huber⁵⁴ for CDTA reaction with $NiEDTA$.

In case of other three ligands the species distribution curves show that the species H_2L is present in not more than 5.0% in the working pH range. Equation (23) in case of all these three ligands can be reduced to Equation (24):

$$k_r \{ [L^{n-}] + [HL^{-(n-1)}] + [H_2L^{-(n-2)}] \} = k_L [L^{n-}] + k_{HL} [HL^{-(n-1)}] \quad \dots (24)$$

Dividing throughout by $[HL^{-(n+1)}]$ one gets,

$$k_r \left\{ \frac{K_n}{[H^+]} + 1 + \frac{[H^+]}{K_{n-1}} \right\} = k_L \frac{K_n}{[H^+]} + k_{HL} \quad \dots (25)$$

where k_L and k_{HL} are the rate constants due to free and mono-protonated forms of ligands respectively while K_n and K_{n-1} are the last and last but one dissociation constants of these ligands (Table II.2).

Table II.9. Effect of pH on the reverse reaction

$-\log [H^+]$	$k'_{\text{obsd}}, \text{MS}^{-1}$	$k_r = \frac{k'_{\text{obsd}}}{[L^{n-}]_T}, \text{S}^{-1}$
1. $\text{Ni}(\text{CN})_4^{2-}$-TMDTA Reaction System		
$[\text{Ni}(\text{CN})_4^{2-}]_i = 4.75 \times 10^{-5} \text{ M}; [\text{TMDTA}^{4-}] = 2.5 \times 10^{-3} \text{ M}; \mu = 0.5 \text{ M}$ (KNO_3); $t = 25^\circ\text{C}$.		
8.9	9.58×10^{-11}	3.83×10^{-8}
9.4	2.11×10^{-10}	8.94×10^{-8}
10.4	3.16×10^{-10}	1.26×10^{-7}
10.7	2.15×10^{-9}	8.60×10^{-7}
10.9	2.20×10^{-9}	8.80×10^{-7}
2. $\text{Ni}(\text{CN})_4^{2-}$-1,2-PDTA Reaction System		
$[\text{Ni}(\text{CN})_4^{2-}]_i = 6.0 \times 10^{-5} \text{ M}; [1,2\text{-PDTA}^{4-}] = 2.5 \times 10^{-2} \text{ M}; \mu = 0.5 \text{ M}$ (NaClO_4); $t = 25^\circ\text{C}$.		
8.95	5.00×10^{-12}	2.00×10^{-10}
9.45	5.75×10^{-12}	2.30×10^{-10}
9.89	8.55×10^{-12}	3.42×10^{-10}
10.40	1.60×10^{-11}	6.40×10^{-10}
10.90	6.50×10^{-11}	2.60×10^{-9}
3. $\text{Ni}(\text{CN})_4^{2-}$-DTPA Reaction System		
$[\text{Ni}(\text{CN})_4^{2-}]_i = 6.4 \times 10^{-5} \text{ M}; [\text{DTPA}^{5-}] = 2.50 \times 10^{-3} \text{ M}; \mu = 0.5 \text{ M}$ (NaClO_4); $t = 25^\circ\text{C}$.		
8.9	8.90×10^{-11}	3.40×10^{-8}
9.4	1.01×10^{-10}	4.14×10^{-8}
9.9	1.10×10^{-10}	4.76×10^{-8}
10.4	1.40×10^{-10}	5.60×10^{-8}
10.9	1.46×10^{-10}	5.84×10^{-8}

...contd.

Table II.9 (contd.)4. $\text{Ni}(\text{CN})_4^{2-}$ -TTHA Reaction System

$$\left[\text{Ni}(\text{CN})_4^{2-}\right]_i = 3.80 \times 10^{-5} \text{ M}; \left[\text{TTHA}^{6-}\right] = 4.18 \times 10^{-3} \text{ M}; \mu = 0.5 \text{ M}$$

(NaClO_4) ; $t = 25^\circ\text{C}$.

8.00	4.00×10^{-10}	9.57×10^{-8}
8.20	3.70×10^{-10}	8.85×10^{-8}
8.50	3.50×10^{-10}	8.37×10^{-8}
9.00	3.31×10^{-10}	7.91×10^{-8}
9.20	4.00×10^{-10}	9.57×10^{-8}
9.50	4.46×10^{-10}	1.07×10^{-7}
10.00	8.90×10^{-10}	2.13×10^{-7}
10.50	1.41×10^{-9}	3.37×10^{-7}
11.00	1.40×10^{-9}	3.35×10^{-7}
11.50	1.41×10^{-9}	3.37×10^{-7}

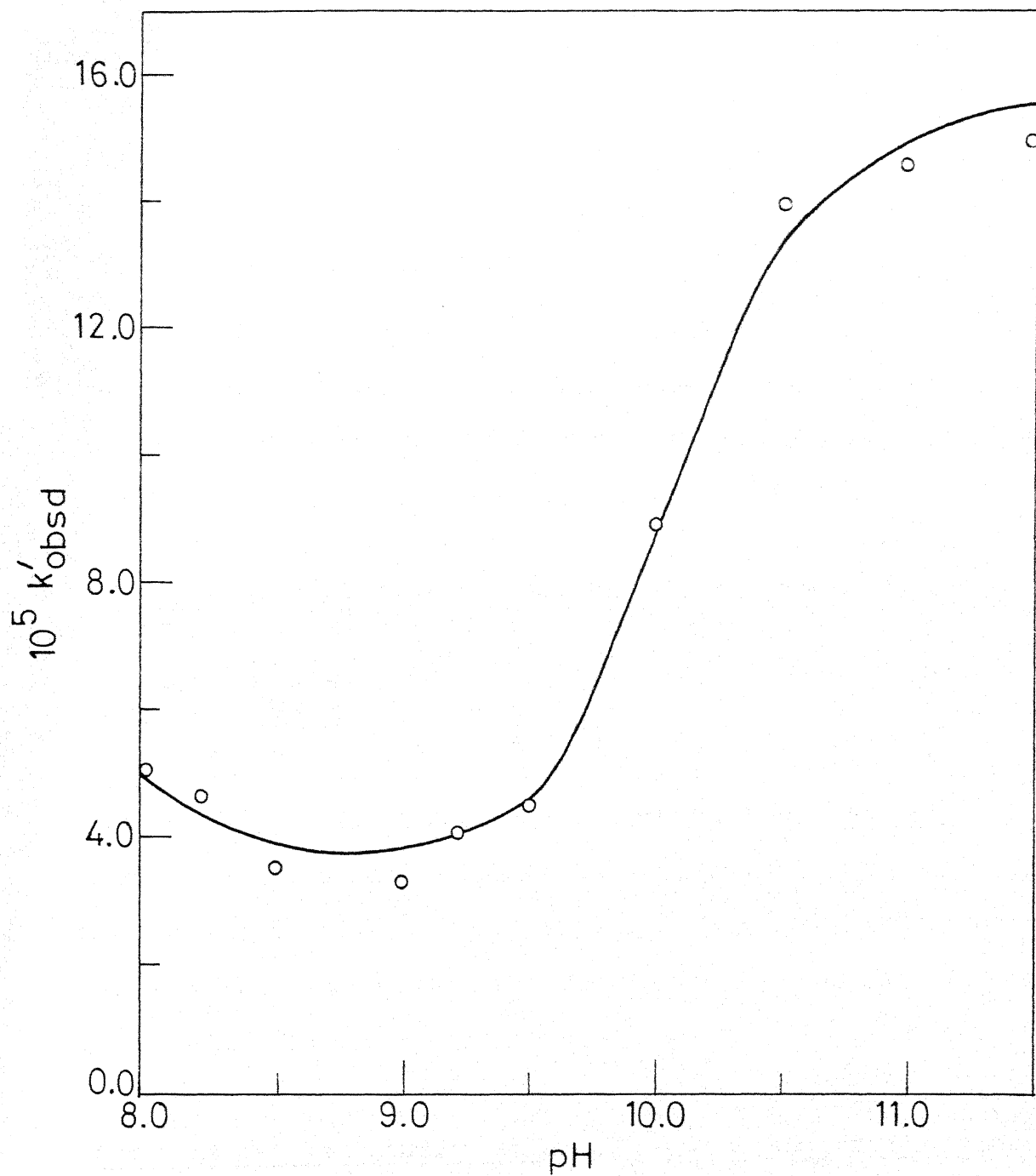


Fig. 11.18 Effect of pH on the Reverse Reaction of $\text{NITHA}^{4-}-\text{CN}^-$ Reaction. The Solid Curve is calculated from Equation (23)

A plot of left hand side of Equation (25) versus $1/[H^+]$ is shown in Figure II.19 and the data also presented in Table II.10. One can get k_L and k_{HL} from the slopes and intercepts of Figure II.19. This type of Equation was also used by Carr and Reilley⁵⁵ to calculate k_L and k_{HL} for the reaction of 1,2-PDTA with PbEDTA and CuEDTA. In case of TMDTA the value of k_{HL} is close to zero with a possible maximum value of $2.0 \times 10^{-8} \text{ s}^{-1}$.

At still lower pH, the rate constants in case of TTHA were resolved as follows. For simplification, the existence of H_3L can be neglected (Fig. II.10) and Equation (23) is transformed to Equation (26):

$$k_r \{ [HL^{5-}] + [H_2L^{4-}] \} = k_{HL} [HL^{5-}] + k_{H_2L} [H_2L^{4-}] \quad \dots (26)$$

$$\text{or } k_r \left\{ 1 + \frac{[H^+]}{K_5} \right\} = k_{HL} + k_{H_2L} \frac{[H^+]}{K_5} \quad \dots (27)$$

From a plot of left hand side of Equation (27) versus $[H^+]/K_5$ (Fig. II.20) one can calculate the values of k_{HL} and k_{H_2L} from the intercept and slope respectively. The agreement between values of k_{HL} calculated from Equations (25) and (27) is very good (Table II.10).

Effect of Na^+ Ion Concentration on Reverse Reaction of Tetra-cyanonickelate Formation

It has been found that the observed rate constants of the reverse reactions change on varying the concentration of Na^+

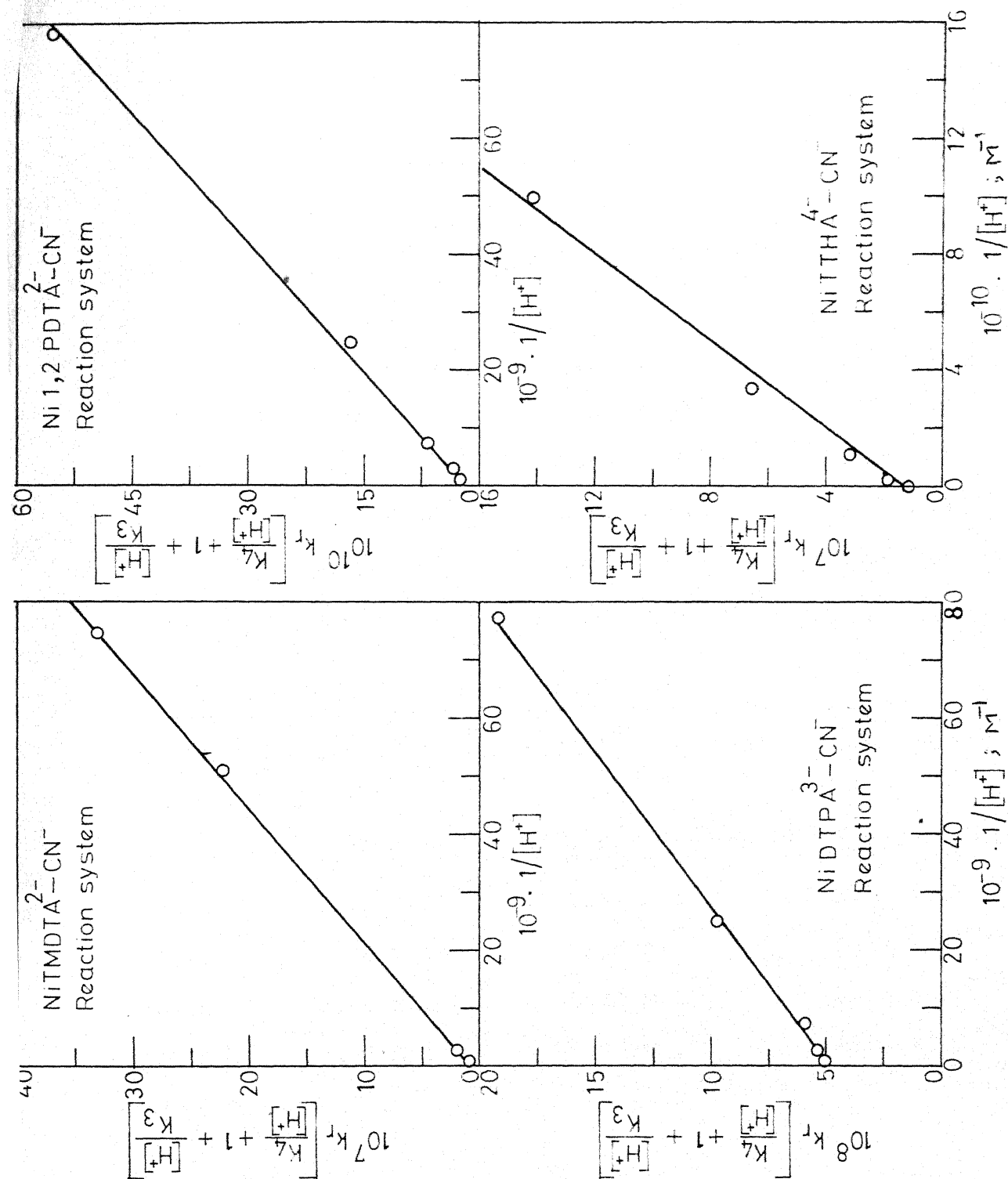


Fig. 11.19 Resolution of Rate Constants k_1 and k_{111} ; plot of left hand side of Equation (25) versus $1/[H^+]$

Table II.10 (contd.)

3. $\text{Ni}(\text{CN})_4^{2-}$ - DTPA^{5-} Reaction System

$[\text{Ni}(\text{CN})_4^{2-}] = 8.10 \times 10^{-5} \text{ M}; [\text{DTPA}]_T = 2.50 \times 10^{-3} \text{ M}; \mu = 0.5 \text{ M}(\text{NaClO}_4);$
 $t = 25^\circ\text{C}.$

8.90	1.26×10^{-9}	7.94×10^8	5.10×10^{-8}
9.40	3.98×10^{-10}	2.51×10^9	5.20×10^{-8}
9.90	1.26×10^{-10}	7.94×10^9	6.09×10^{-8}
10.40	3.98×10^{-11}	2.51×10^{10}	9.80×10^{-8}
10.90	1.26×10^{-11}	7.94×10^{10}	19.51×10^{-8}

Calcd $k_L = 6.37 \times 10^{-8} \text{ s}^{-1}; k_{HL} = 4.75 \times 10^{-8} \text{ s}^{-1}.$

4. $\text{Ni}(\text{CN})_4^{2-}$ - TTHA^{6-} Reaction System

$[\text{Ni}(\text{CN})_4^{2-}] = 3.80 \times 10^{-5} \text{ M}; [\text{TTHA}^{6-}]_T = 4.18 \times 10^{-3} \text{ M}; \mu = 0.5 \text{ M}(\text{NaClO}_4);$
 $t = 25^\circ\text{C}.$

9.50	3.16×10^{-10}	3.16×10^9	2.11×10^{-7}
10.00	1.00×10^{-10}	1.00×10^{10}	3.40×10^{-7}
10.50	3.10×10^{-11}	3.16×10^{10}	7.03×10^{-7}
11.00	1.00×10^{-11}	1.00×10^{11}	1.40×10^{-6}
11.50	3.16×10^{-12}	3.16×10^{11}	3.71×10^{-6}
$-\log [\text{H}^+]$	$[\text{H}^+]$	$[\text{H}^+]/K_5$	$k_r \left\{ 1 + \frac{[\text{H}^+]}{K_5} \right\}$
8.00	1.00×10^{-8}	27.59	3.43×10^{-6}
8.20	6.31×10^{-9}	17.38	2.05×10^{-6}
8.50	3.16×10^{-9}	8.72	8.13×10^{-7}
9.00	1.00×10^{-9}	2.75	2.97×10^{-7}
9.20	6.31×10^{-10}	1.74	2.93×10^{-7}

Calcd $k_L = 4.00 \times 10^{-7} \text{ s}^{-1}; k_{HL} = 1.00 \times 10^{-7} \text{ s}^{-1}$ and
 $k_{H_2L} = 1.25 \times 10^{-7} \text{ s}^{-1}.$

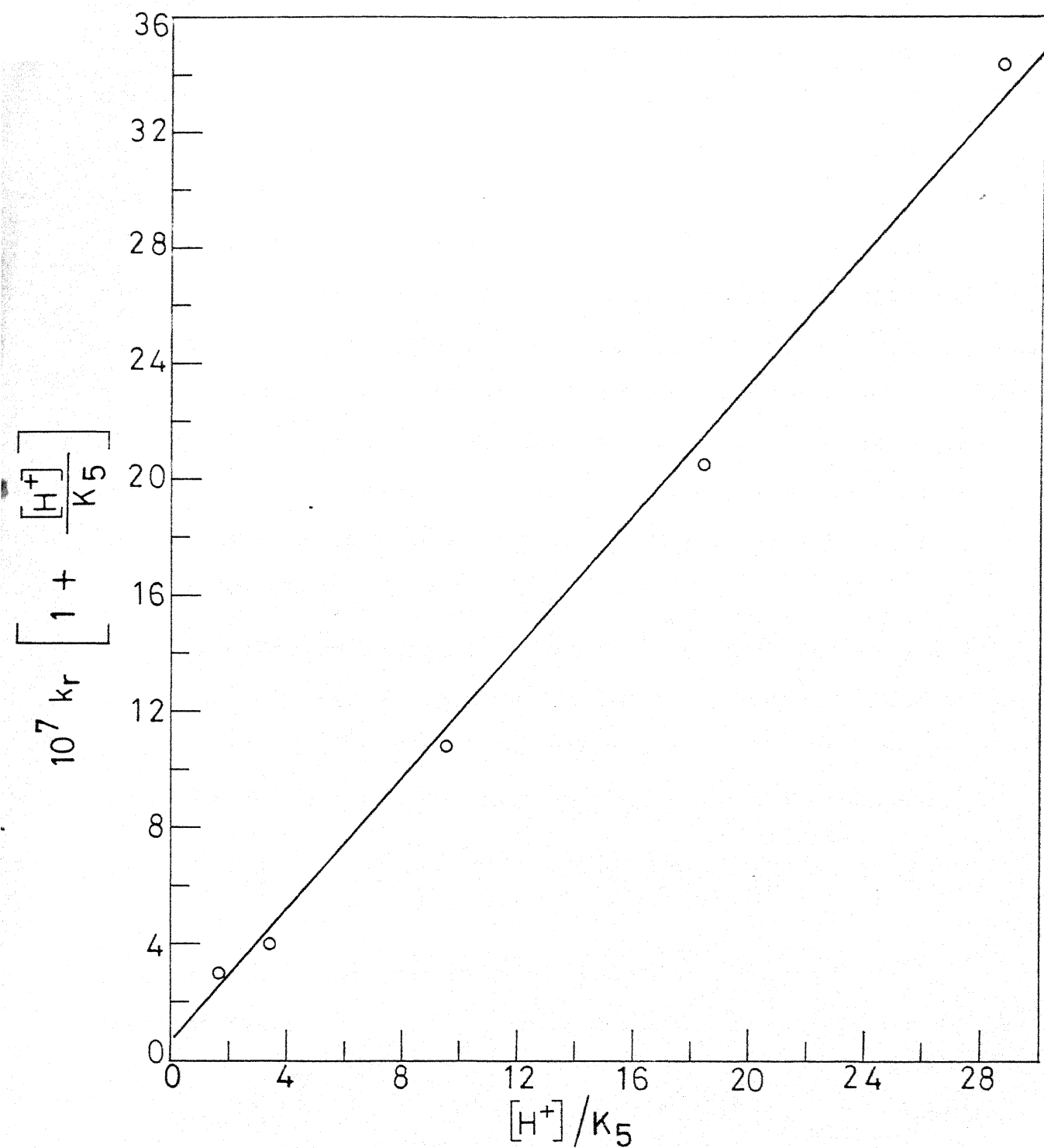


Fig. 11.20 Resolution of Rate Constants k_{HL} and k_{H_2L} ; Plot of left hand side of Equation (27) versus $[H^+]/K_5$

added to control the ionic strength of the reaction medium (Table II.11 and Figure II.21). Such behaviour has also been observed previously by Sudmeir and Reilley,⁵⁶ Kula and Reed⁵⁷ and Carr et al.⁵⁸ This is, undoubtedly, due to formation of weak complexes like NaL^{3-} which in turn could decrease the concentration of free anion of aminocarboxylate. Alternatively the observed decrease could also be due to a slower reaction between NaL^{-n+1} and $\text{Ni}(\text{CN})_4^{2-}$ than between L^{n-} and the latter. Sodium complexes of some aminocarboxylates have been reported in literature.^{34,59-63} Though not much is known about the structural features of these sodium complexes, some NMR studies⁶⁴ suggest the involvement of nitrogen atoms of EDTA in alkali metal complex formation.

In order to determine whether the rate decrease is solely due to a decrease in concentration of aminocarboxylate anion or whether NaL^{-n+1} is also reacting to a greater or lesser extent, the observed rate constants were resolved as below:

$$k_r [\text{L}]_T = k_L [\text{L}^{n-}] + k_{\text{HL}} [\text{HL}^{-n+1}] + k_{\text{NaL}} [\text{NaL}^{-n+1}] \quad \dots (28)$$

This expression on algebraic manipulation transforms to Equation (29):

$$k_r \left\{ 1 + \frac{[\text{H}^+]}{K_{\text{HL}}} + K_{\text{NaL}} [\text{Na}^+] \right\} = k_L + k_{\text{HL}} \frac{[\text{H}^+]}{K_{\text{HL}}} + k_{\text{NaL}} K_{\text{NaL}} [\text{Na}^+] \quad \dots (29)$$

A plot of left hand side of Equation (29) versus $[\text{Na}^+]$ when

Table II.11. Effect of sodium ion concentration on the reverse reaction

temp = 25°C; pH = 11.0±0.1; μ = 0.5 M (KNO₃ + NaNO₃)

$[\text{NaNO}_3], \text{ M}$	$k'_{\text{obsd}}, \text{ MS}^{-1}$
<u>1. Ni(CN)₄²⁻ - TMDTA⁴⁻ Reaction System</u>	
$[\text{Ni(CN)}_4^{2-}] = 4.05 \times 10^{-5} \text{ M}; [\text{TMDTA}^{4-}]_{\text{T}} = 2.50 \times 10^{-3} \text{ M.}$	
0.1	1.0×10^{-9}
0.2	7.56×10^{-10}
0.3	5.36×10^{-11}
0.5	3.55×10^{-10}
calcd $k_{\text{L}} = 1.27 \times 10^{-6} \text{ s}^{-1}; k_{\text{NaL}} = 8.17 \times 10^{-8} \text{ s}^{-1}.$	
<u>2. Ni(CN)₄²⁻ - 1,2-PDTPA⁴⁻ Reaction System</u>	
$[\text{Ni(CN)}_4^{2-}] = 6.65 \times 10^{-5} \text{ M}; [1,2\text{-PDTPA}^{4-}]_{\text{T}} = 2.50 \times 10^{-3}$	
0.0	3.94×10^{-9}
1.0	2.25×10^{-10}
0.25	7.37×10^{-11}
calcd $k_{\text{L}} = 2.70 \times 10^{-7} \text{ s}^{-1}; k_{\text{NaL}} = 2.10 \times 10^{-7}.$	
<u>3. Ni(CN)₄²⁻ - DTPA⁵⁻ Reaction System</u>	
$[\text{Ni(CN)}_4^{2-}] = 5.20 \times 10^{-5} \text{ M}; [\text{DTPA}^{5-}]_{\text{T}} = 6.25 \times 10^{-3} \text{ M.}$	
0.0	1.89×10^{-9}
0.05	9.88×10^{-10}
0.10	7.59×10^{-10}
0.20	5.54×10^{-10}
0.30	3.90×10^{-10}
0.42	2.57×10^{-10}
calcd $k_{\text{L}} = 5.90 \times 10^{-7} \text{ s}^{-1}; k_{\text{NaL}} = 1.36 \times 10^{-8} \text{ s}^{-1}.$	

...contd.

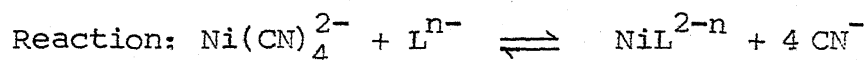
Table II.11 (contd.)

4. $\text{Ni}(\text{CN})_4^{2-}$ - TTHA^{6-} Reaction System

$[\text{Ni}(\text{CN})_4^{2-}]$	$= 3.50 \times 10^{-5} \text{ M};$	$[\text{TTHA}^{6-}]_T$	$= 8.35 \times 10^{-3} \text{ M};$
0.05		3.28×10^{-9}	
0.10		2.90×10^{-9}	
0.30		2.30×10^{-9}	
0.50		2.00×10^{-9}	

Calcd $k_L = 8.30 \times 10^{-7} \text{ s}^{-1};$ $k_{\text{NaL}} = 3.40 \times 10^{-8} \text{ s}^{-1}$

Table II.12. Rate constants of reverse reactions and stability constants of sodium aminocarboxylate complexes



Aminocarboxylate L	$K_4^{-1} k_{-3}; \text{ s}^{-1}$	$\log K_{\text{NaL}}$	Ref.
TMDTA	$(1.96 \pm 0.17) \times 10^{-7}$	1.08	30
1,2-PDTA	$(3.03 \pm 0.20) \times 10^{-9}$	2.20	33, 34
EDTA	2.20×10^{-8}	1.61 1.45	67 58, 59
DTPA	$(5.00 \pm 0.45) \times 10^{-8}$	1.37	36
TTHA	$(3.08 \pm 0.17) \times 10^{-7}$	1.00	41
EGTA	$(7.30 \pm 0.60) \times 10^{-8}$	1.38	63

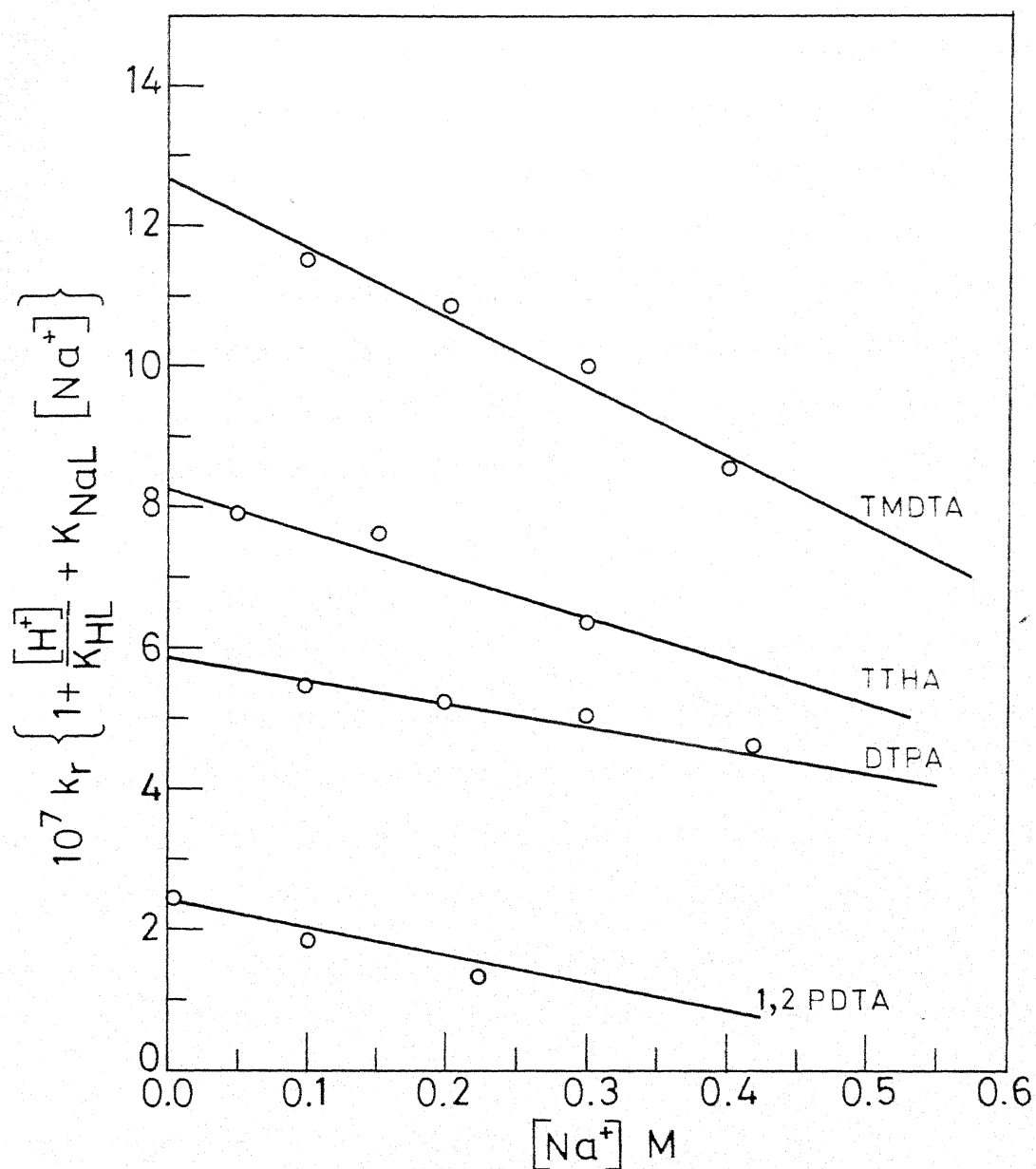


Fig. 17.21 Resolution of Rate Constants k_L and k_{NaL} ; Plot of left hand side of Equation (29) versus $[Na^+]$.

the ionic strength is held constant by addition of KNO_3 is shown in Figure II.21. From the slope and intercept of this plot one can calculate k_{NaL} and k_{L} for all the four aminocarboxylates. Here a simplifying assumption has been made that $k_{\text{HL}} \frac{[\text{H}^+]}{K_{\text{HL}}}$ term can be ignored at pH 11.0. Also the complexing ability of K^+ with aminocarboxylates has been neglected ($\log K_{\text{KEDTA}} = 0.96$, cf. $\log K_{\text{NaEDTA}} = 1.61$, $\log K_{\text{NaPDTA}} = 2.20$)*. The resolved rate constants corresponding to NaL^{-n+1} reaction and L^{n-} reaction are given in Table II.11. These values indicate that NaL^{-n+1} is less reactive than L^{n-} itself.

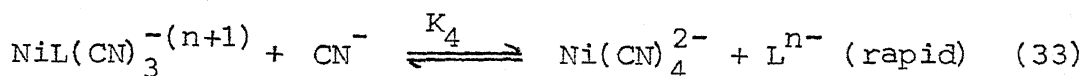
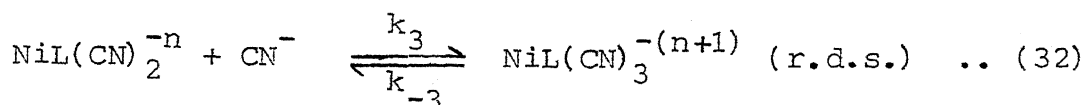
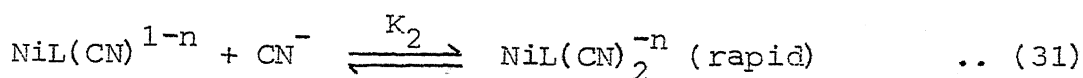
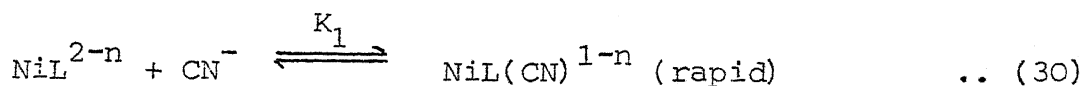
II.5 DISCUSSION

The experimental observations on the rates of forward and reverse reactions lead to a mechanism proposed earlier by Margerum et al.³⁻⁵ and supported by others⁷ but in disagreement with the mechanism assumed by Stara & Kopanica⁸ who had investigated the NiTTA reaction with cyanide earlier. A reinvestigation of this reaction was necessitated further because their results could not be reproduced. For example, first and second order dependence was observed in this work while they reported only third order dependence under similar conditions. They also failed to incorporate inverse first order dependence in their reverse rate expression although they noticed that the reverse rate is suppressed by presence of free cyanide. The fallacies in their experimental work and erroneous mechanism have been

*See Refs. 33, 34, 65-67.

discussed at length in a recent communication from this laboratory.⁵²

The reactions investigated in this work proceed by a mechanism given earlier (Eqn. 11-14) but is reproduced below for ready reference.



An expression that reflects the variable order of forward rate on cyanide concentration is given in Equation (34):

$$k_{\text{obsd}} = \frac{K_1 K_2 k_3 [\text{CN}^-]^3}{1 + K_1 [\text{CN}^-] + K_1 K_2 [\text{CN}^-]^2} \quad \dots (34)$$

This expression reduces to a third, second and first order expression in cyanide dependence at low medium and high cyanide concentrations respectively. For the reactions under discussion only first and second order dependence has been observed experimentally (Fig. II.11), but in case of EDDA, NTA and HPDTA³ a third order dependence was also verified.

One can proceed now to derive the experimental rate law for reverse reaction by applying steady state treatment to the

intermediate produced in the rate determining step, namely $\text{NiL}(\text{CN})_3^{-(n+1)}$. Rate of formation of this intermediate is given by Equation (35), which may be set to zero. Thus

$$\begin{aligned}
 -\frac{d[\text{NiL}(\text{CN})_3^{-(n+1)}]}{dt} &= k_3 [\text{NiL}(\text{CN})_2^{-n}] [\text{CN}^-] - k_{-3} [\text{NiL}(\text{CN})_3^{-(n+1)}] \\
 &\quad + k_{-4} [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}] + k_4 [\text{NiL}(\text{CN})_3^{-(n+1)}] [\text{CN}^-] \\
 &= 0 \\
 \text{so } [\text{NiL}(\text{CN})_3^{-(n+1)}] &= \frac{k_3 [\text{NiL}(\text{CN})_2^{-n}] [\text{CN}^-] + k_{-4} [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}]}{k_4 [\text{CN}^-] + k_{-3}} \quad \dots (35)
 \end{aligned}$$

$$\begin{aligned}
 -\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} &= k_{-3} [\text{NiL}(\text{CN})_3^{-(n+1)}] \\
 &= \frac{k_{-3} \{ k_3 [\text{NiL}(\text{CN})_2^{-n}] [\text{CN}^-] + k_{-4} [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}] \}}{k_4 [\text{CN}^-] + k_{-3}} \\
 &\quad \dots (36)
 \end{aligned}$$

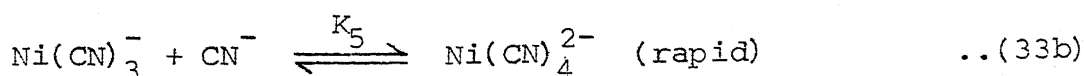
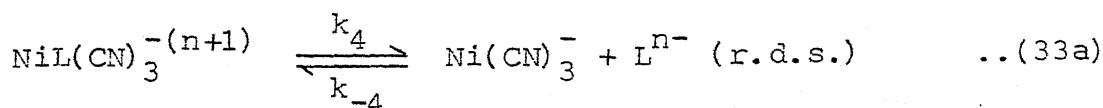
In presence of excess ligand, the first term in the numerator can be ignored. Our results on forward and reverse rate study show that the fourth step is fast compared to the third and values of k_4 (also k_{-4}) must be quite large. Thus even though $[\text{CN}^-]$ may be small $k_4 [\text{CN}^-]$ may still be quite large compared to k_{-3} which may be omitted in the denominator. With these assumption Equation (36) reduces to (37):

$$\begin{aligned}
 \text{rate} = -\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} &= \frac{k_{-3} k_{-4}}{k_4} \cdot \frac{[\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}]}{[\text{CN}^-]} \\
 &= \frac{k_r [\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}]}{[\text{CN}^-]} \quad \dots (37)
 \end{aligned}$$

where $k_r = \frac{k_{-3} k_{-4}}{k_4}$.

This rate expression is in conformity with the observed rate law for reverse reaction given in Equation (9) .

A kinetically equivalent alternative in which reaction (33) is replaced by two other steps (Equations 33a and 33b) :



has been considered but found to be unacceptable for the following reasons. Firstly, the low activation energy values for forward reaction and high values for reverse reaction for all the ligands (Tables II.5 and II.6) favour the postulated mechanism where no bond breaking is involved in the rate determining step of the forward reaction but bond breaking is involved in the reverse reaction. It should have been the other way round in the alternative mechanism. Further, the large entropy decrease in general, in forward reactions also strengthens the proposed mechanism because there is a decrease in the number of chemical species in the rate determining step. Secondly, the stability constant of $\text{Ni}(\text{CN})_3^-$ has been estimated¹¹ to be of the order of 2×10^{16} . This would give the value of $K_5 (= \beta_4/\beta_3)$ of Equation (33b) equal to 1.25×10^{14} . The dissociation rate constant k_{-5} of $\text{Ni}(\text{CN})_4^{2-}$ has been determined¹ to be equal to $4.8 \times 10^{-4} \text{ s}^{-1}$ between pH 3.0-8.0 in presence of I_2 as scavenger

for CN^- ion in which case the dissociation is not complicated by reversibility. The value of this dissociation constant k_{-5} at high pH is expected to be even lower. The observed rate constants k_r for the overall reverse reaction $k_{-4} \cdot K_5^{-1}$ of Equation (33b) or $k_{-3} \cdot K_4^{-1}$ of Equation (32) are listed in Table II.4. From these values k_{-4} can be calculated to be

$$k_{-4} = \frac{1.96 \times 10^{-7} \times 10^{30.4}}{2 \times 10^{16}} = 9.85 \times 10^7 \text{ (for TMDTA)}$$

$$k_{-4} = \frac{3.03 \times 10^{-9} \times 10^{30.4}}{2 \times 10^{16}} = 3.80 \times 10^5 \text{ (for 1,2-PDTA)}$$

$$k_{-4} = \frac{4.78 \times 10^{-8} \times 10^{30.4}}{2 \times 10^{16}} = 6.00 \times 10^6 \text{ (for DTPA)}$$

$$k_{-4} = \frac{3.08 \times 10^{-7} \times 10^{30.4}}{2 \times 10^{16}} = 3.87 \times 10^7 \text{ (for TTHA)}$$

These values are many orders of magnitude higher than the k_{-5} value ($4.8 \times 10^{-4} \text{ s}^{-1}$). Thus the rate determining step in alternative mechanistic scheme should shift to reaction (33b) resulting in fourth order dependence in cyanide which is contrary to experimental observation, hence the alternative scheme is not acceptable.

As has been stated before only first and second order dependence in cyanide was observed in this work while first, second and third order dependence was observed in case of EDDA and NTA.³ First order dependence in cyanide gives k_3 while

second and third orders give K_2k_3 and $K_1K_2k_3$ respectively from the rate data.

An algebraic expression (Equation 40) which gives K_1K_2 in terms of known stability constants and rate constants is derived below:

$$\text{forward rate} = k_3 [\text{NiL}(\text{CN})_2^{n-}] [\text{CN}^-] = K_1K_2k_3 [\text{NiL}^{2-n}] [\text{CN}^-]^3 \quad \dots (38)$$

$$\text{reverse rate} = k_{-3} [\text{NiL}(\text{CN})^{-(n+1)}] = k_{-3}K_4^{-1} \frac{[\text{Ni}(\text{CN})_4^{2-}] [\text{L}^{n-}]}{[\text{CN}^-]} \quad \dots (39)$$

Equating forward and reverse rates, multiplying and dividing the right hand side by $[\text{Ni}^{2+}]$, followed by simple algebraic manipulations one obtains

$$K_1K_2 = \frac{K_4^{-1} \cdot k_{-3} \cdot \beta_4}{k_3 \cdot K_{\text{NiL}}} \quad \dots (40)$$

where β_4 is the stability constant of $\text{Ni}(\text{CN})_4^{2-}$. Equation (40) may be transformed to

$$K_1K_2k_3 = \frac{K_4^{-1} \cdot k_{-3} \cdot \beta_4}{K_{\text{NiL}}} \quad \dots (41)$$

$$\text{or} \quad \log K_1K_2k_3 = \log K_4^{-1} \cdot k_{-3} \cdot \beta_4 - \log K_{\text{NiL}} \quad \dots (42)$$

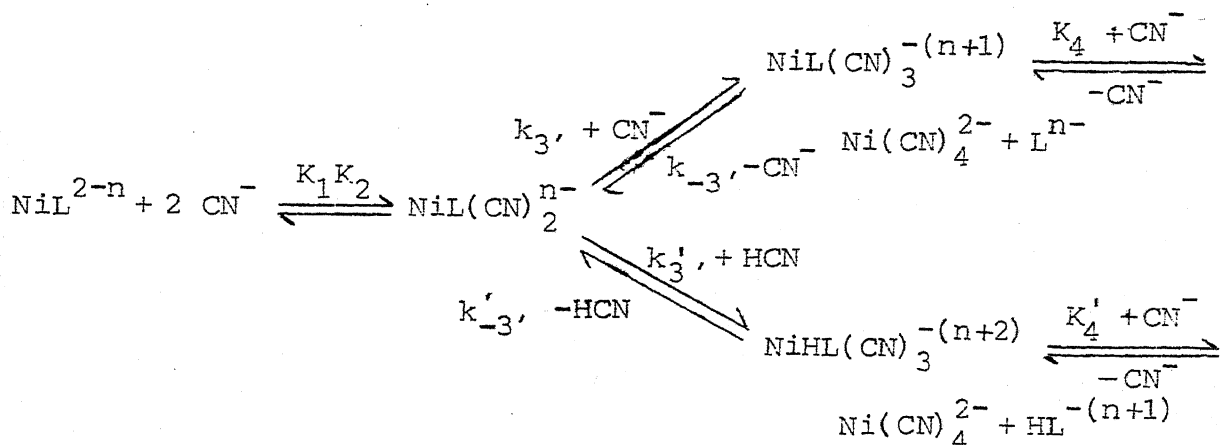
so the observed rate should to be inversely proportional to K_{NiL} . This is shown to be true (Figure II.27) for a number of aminocarboxylates investigated so far. The negative slope of the straight line of Figure II.27 is a little more than unity.

Margerum & coworkers³ attempted to add an electrostatic correction term K_{elec} to compensate for the different charges. The values of K_{elec} were estimated using distances obtained from the center of nickel atom to the center of remote carboxylate group. The data were found to be overcorrected probably because the approximately 0.1 M Na^+ in solution will have some specific association with free aminocarboxylate group.

The critical step in the nickel system appears to be conversion of an octahedral (or tetragonal) to a square planar complex having three cyanides around Ni^{2+} in the rate determining step. The fourth cyanide adds quite rapidly to this displacing the remaining attached glycinate segment of aminocarboxylate complexes and finally producing $Ni(CN)_4^{2-}$. The details of mechanistic scheme are outlined in Figure II.24.

A brief comment on the pH dependence of the reaction rates will be in order. The observed first order rate constants start decreasing markedly below pH 10.0 (Fig. II.16) which is due to formation of a poor nucleophile HCN. The slope of 1 in this figure between pH 7 to 9 shows that one molecule of HCN is a reactant as well as cyanide below pH 9.0. Above this pH the value of k_{obsd} begins to level off as would be expected from the value of the pK_a (= 9.0) of HCN because CN^- is the principal reactive chemical species above this pH. It is believed that intramolecular proton transfer from HCN to the more basic nitrogen of the unfolding glycinate group occurs, and facilitate the unwrapping of aminocarboxylate from nickel(II). This proton

transfer can not be to the carboxylate group as these groups are more acidic and the proton will transfer to the solvent. Thus two parallel reactions are observed in the pH range 7 to 9.



It can be ascertained from the species distribution of NiTTHA system (Figure II.10) that NiL converts mostly to NiHL at pH below 8.0. Yet no deviation was observed from the expected slope below pH 8.0 (Figure II.16). One would conclude from this that the reactivities of NiTTHA and Ni(HTTHA) are comparable. This is not unexpected when one considers the possible structure of the latter if one assumes that this is similar to the structure of Cu(HTTHA) proposed by Martell²⁶ (Figure II.22). Since the proton is far removed from the actual binding sites where substitution occurs, the rate of substitution remains same for the unprotonated or monoprotonated complex. At low pH the main reactant becomes Ni(HTTHA)³⁻ instead of Ni(TTHA)⁴⁻ and in the third step HCN is a reactant instead of CN⁻ below pH 9.0. Based on considerations of electroneutrality, stoichiometry and species distribution of TTHA one can write a two path mechanism

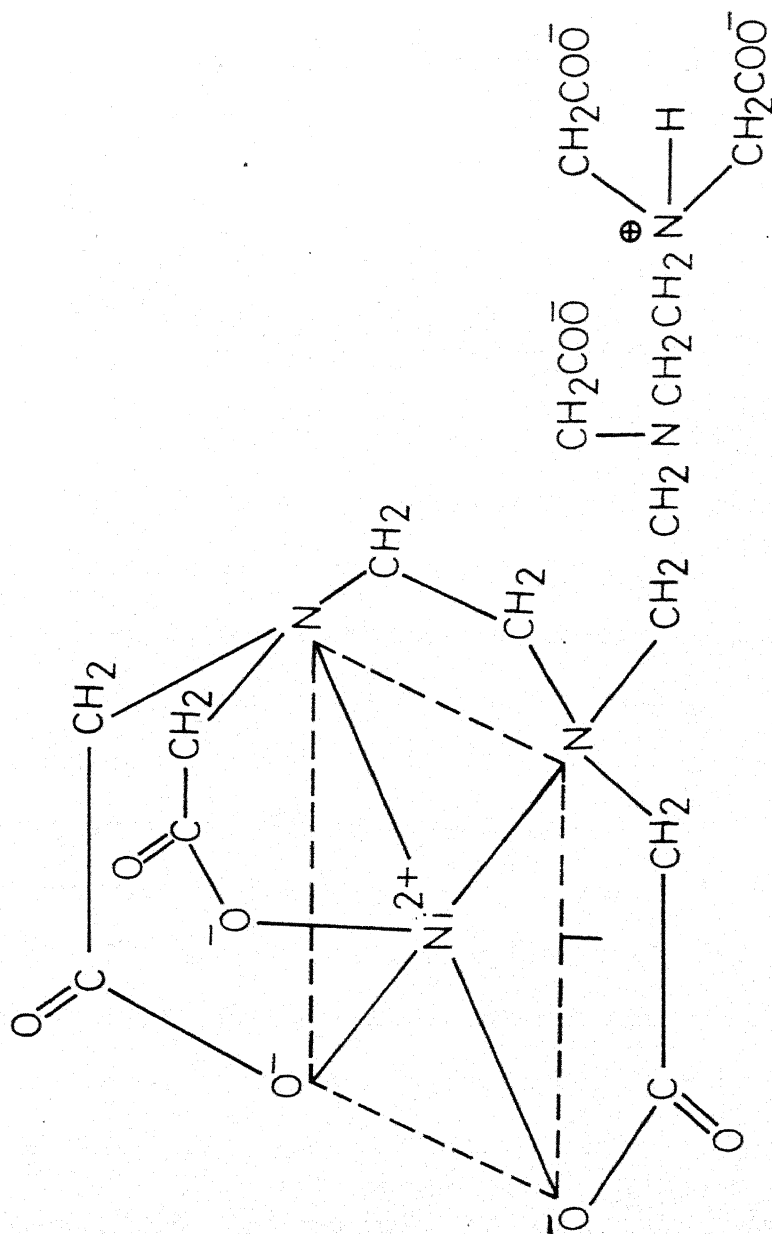
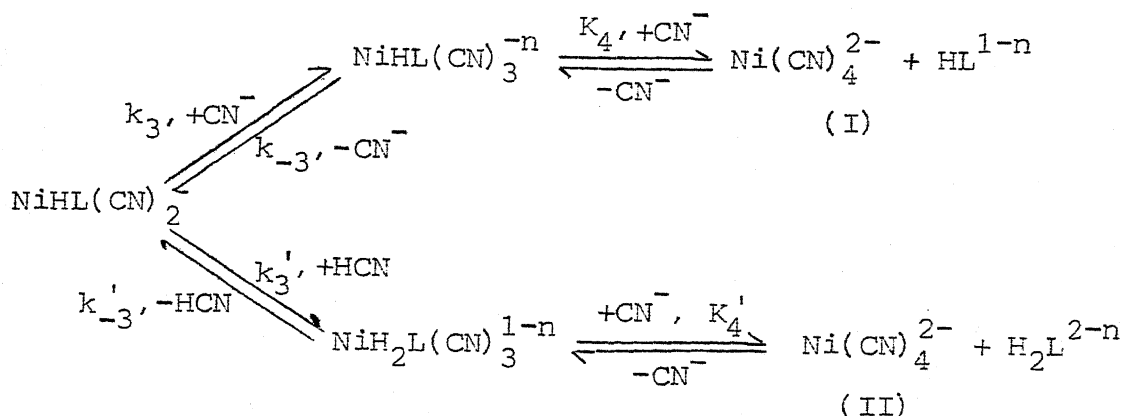


Fig. 11.22 Proposed Structure of $\text{Ni}(\text{HTTMA})^{3-}$ Complex
(cf. $\text{Cu}(\text{HTTMA})^{3-}$; Ref. 26)

for this case as given below. The first two steps are similar to above scheme. In this scheme L represents only TTHA:



The observed rate constants for the reverse reactions (k'_{obsd}) decrease as pH decreases. This is due to the formation of protonated ligand species. In general, the monoprotinated species predominate (Figures II.6 to II.10) in the pH range of investigation of reverse rates that is pH 7 to 9. Hence the rate decreases due to formation of monoprotinated forms of aminocarboxylates which are poor nucleophiles. An exception to this general trend is the TTHA⁶⁻ reaction where the rate increases after an initial decrease at lower pH value (Figure II.18). From this behaviour it is concluded that diprotinated forms of TTHA plays a more dominant role at low pH values.

Comparison of reverse rates of various aminocarboxylates in sodium perchlorate medium shows that reverse rate constants are varying from one ligand to another as their stability constants with Na⁺ are varying.⁶⁸ It was possible to correlate the reverse rates ($K_4^{-1} \cdot k_{-3}$) with K_{NaL} (Figure II.23 and

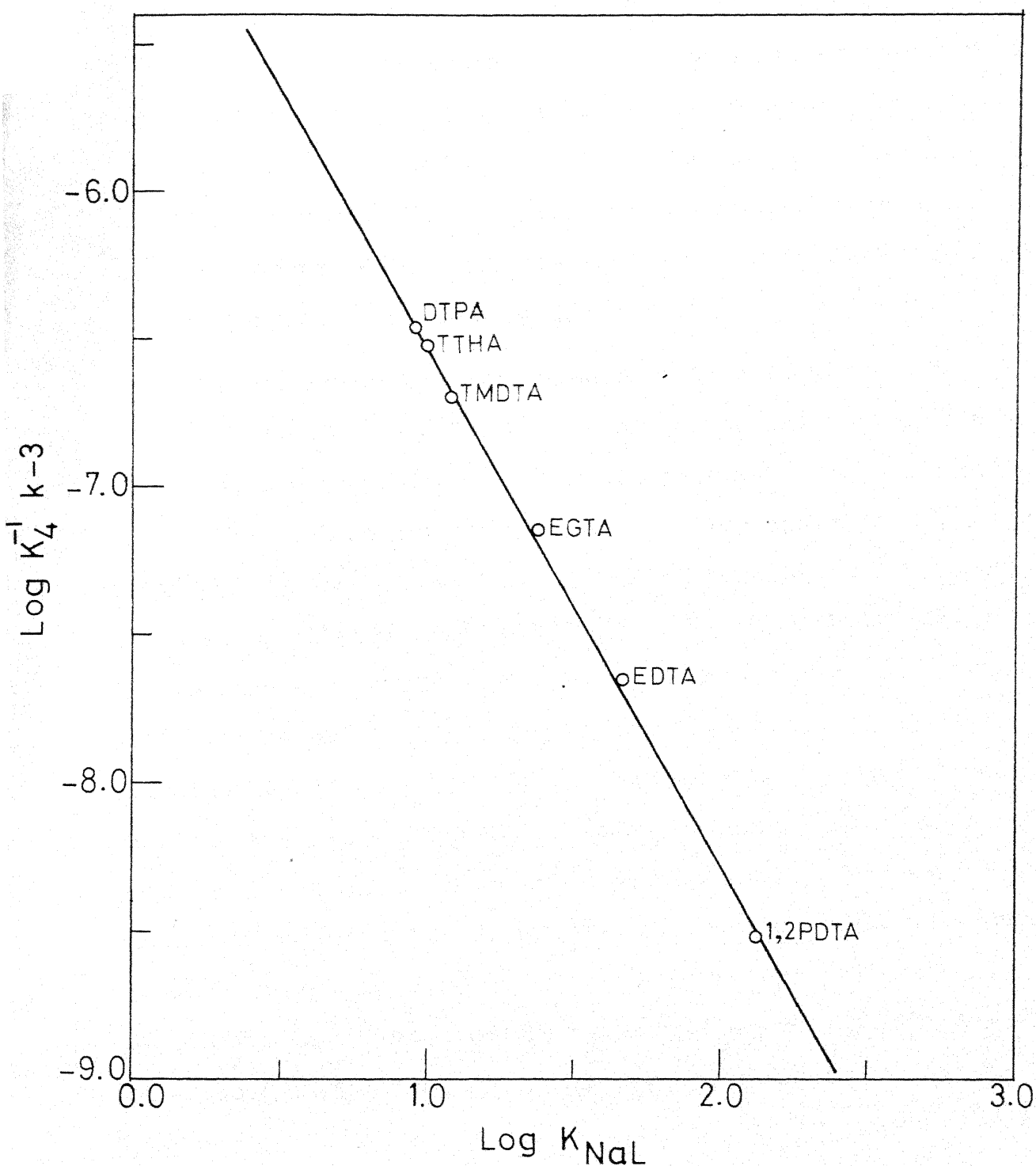


Fig. 11.23 Correlation Between Reverse Rate Constants $K_4^{-1} k_{-3}$ and Stability Constants of Sodium Aminocarboxylate Complexes (K_{NaL}). Temp = 25°C; pH = 11.0; $\mu = 0.5 \text{ M}$

Table II.12. This matter has been treated in the Experimental Section. The conclusion is that NaL^{1-n} is less reactive than L^{n-} . It is also interesting to note that a linear relationship exists between $k_4^{-1} \cdot k_{-3}$ (the reverse rate constant) and K_{NaL} of individual aminocarboxylates. This relationship makes it possible to predict the K_{NaL} from a knowledge of rate data. Coombs⁶⁹ has tried to correlate the $k_4^{-1} k_{-3}$ with charge on free aminocarboxylates but only qualitatively.

The behaviour of three structurally similar ligands viz., EDTA^{4-} , $1,2\text{-PDTA}^{4-}$ and TMDTA^{4-} is now compared. All the ligands show the same mechanism but the rate constants are quite different. The rate of substitution follows the order $\text{TMDTA}^{4-} > \text{EDTA}^{4-} > 1,2\text{-PDTA}^{4-}$ (Table II.13). The rather large difference in rates of NiTMDTA^{2-} ($K = 10^{18.07}$) and Ni-1,2-PDTA^{2-} ($K = 10^{19.6}$) on one hand and NiEDTA^{2-} ($K = 10^{18.47}$) and Ni-1,2-PDTA^{2-} on the other can be explained on the basis of two reasons: (i) The stability constants of the three complexes are quite different and (ii) the large difference between reactions of apparently similar complexes can be attributed to the requirement of methyl group and its effect on the course of reaction mechanism. Carr et al.⁵⁸ have demonstrated that the methyl group of a fully coordinated $1,2\text{-PDTA}^{4-}$ molecule tends to keep the dentate groups in a position favourable for binding by causing rotational hindrance to the iminodiacetate segment away from central metal ion. This should result in an additional potential energy barrier which must be overcome before the formation of the

Table II.13. Summary of rate and equilibrium constants calculated from kinetic data

NiL ²⁻ⁿ	NiTMDDTA	Ni-1, 2-PDTPA	NiDTPA	NiTTTA
$K_3, M^{-1}S^{-1}$	$(4.38 \pm 0.35) \times 10^{-1}$	$(5.70 \pm 0.81) \times 10^{-3}$	$(3.27 \pm 0.22) \times 10^{-1}$	$(1.39 \pm 0.05) \times 10^{-1}$
$K_2K_3, M^{-2}S^{-1}$	$(2.85 \pm 0.31) \times 10^1$	$(1.77 \pm 0.12) \times 10^{-2}$	(5.53 ± 0.77)	$(1.24 \pm 0.06) \times 10^2$
$K_1K_2K_3, M^{-3}S^{-1}$	5.27×10^5	2.06×10^{-2}	7.52×10^2	1.50×10^5
$K_4^{-1}K_{-3}, S^{-1}(NaClO_4)$	$(1.96 \pm 0.21) \times 10^{-7}$	$(3.03 \pm 0.24) \times 10^{-9}$	$(4.78 \pm 0.6) \times 10^{-8}$	$(3.08 \pm 0.17) \times 10^{-7}$
$K_4^{-1}K_{-3}, S^{-1}(KNO_3)$	$(7.36 \pm 0.92) \times 10^{-7}$	-	-	-
K_1, M^{-1}	1.85×10^4	1.16×10^4	1.36×10^2	1.20×10^3
K_2, M^{-1}	6.51×10^1	3.10	1.69×10^1	9.00×10^2
K_1K_2, M^{-2}	1.20×10^6	3.61×10^4	2.30×10^3	1.07×10^6
$K_2K_3, M^{-2}S^{-1}$	2.85×10^1	$(1.20 \times 10^{-1})^a$	$(51.57)^a$	120.0
$K_2K_3', M^{-2}S^{-1}$	1.43×10^1	$(0.55 \times 10^{-1})^a$	$(13.30)^a$	16.7
$K_r(CN)_4^{2-}, S^{-1}$	7.80×10^{-7}	4.67×10^{-9}	6.37×10^{-8}	4.00×10^{-7}
$K_r(CN)_4^{2-}, S^{-1}$	2.00×10^{-8}	1.20×10^{-10}	4.75×10^{-8}	1.00×10^{-7}
$K_r(H_2L)_4^{2-}, S^{-1}$	-	-	-	1.25×10^{-7}
$K_r(NaL), S^{-1}$	8.17×10^{-8}	-	1.36×10^{-8}	3.40×10^{-8}

a, temp = 40°C.

intermediate proposed in the reaction mechanism. Also, the basicity of nitrogen atoms in 1,2-PDTA is enhanced (as compared to EDTA and TMDTA) due to electron donating character of the methyl group. The strength of metal-nitrogen bond in the 1,2-PDTA complex would be, therefore, stronger than in EDTA complex. Both these effects combine to reduce the forward reaction rate in case of 1,2-PDTA in comparison to EDTA or TMDTA. A similar effect was seen in the rate constants of NiIDA and NiMIDA reactions with CN^- . The lowering of rates can, therefore, be rationalized.

X-ray study of NiEDTA^{2-} by Smith and Hoard⁷⁰ showed that EDTA is penta-coordinated in the solid state. Penta-coordination by EDTA in solution has been indirectly assumed in many proposed kinetic schemes. It has been verified by Everhart and Evilia⁷¹ for EDTA, TMDTA and PDTA complexes of Ni(II) in aqueous solution also. A structure for NiDTPA has been proposed by Bailer⁷² and for CuTTHA by Martell.²⁶ Structure of NiTTHA may be assumed to be same as that of CuTTHA . It is now possible to visualize the step by step intermediates in the reactions under investigation. To take the specific example of TMDTA the first cyanide displaces the weakly bound water and following steps are shown in Figure II.24. Kinetic data shows evidence for three cyanides around nickel ion in the rate determining step. This grouping of donors is sufficient to cause a ligand field strong enough to convert an octahedral grouping to a square planar configuration. Once this is achieved the substitution

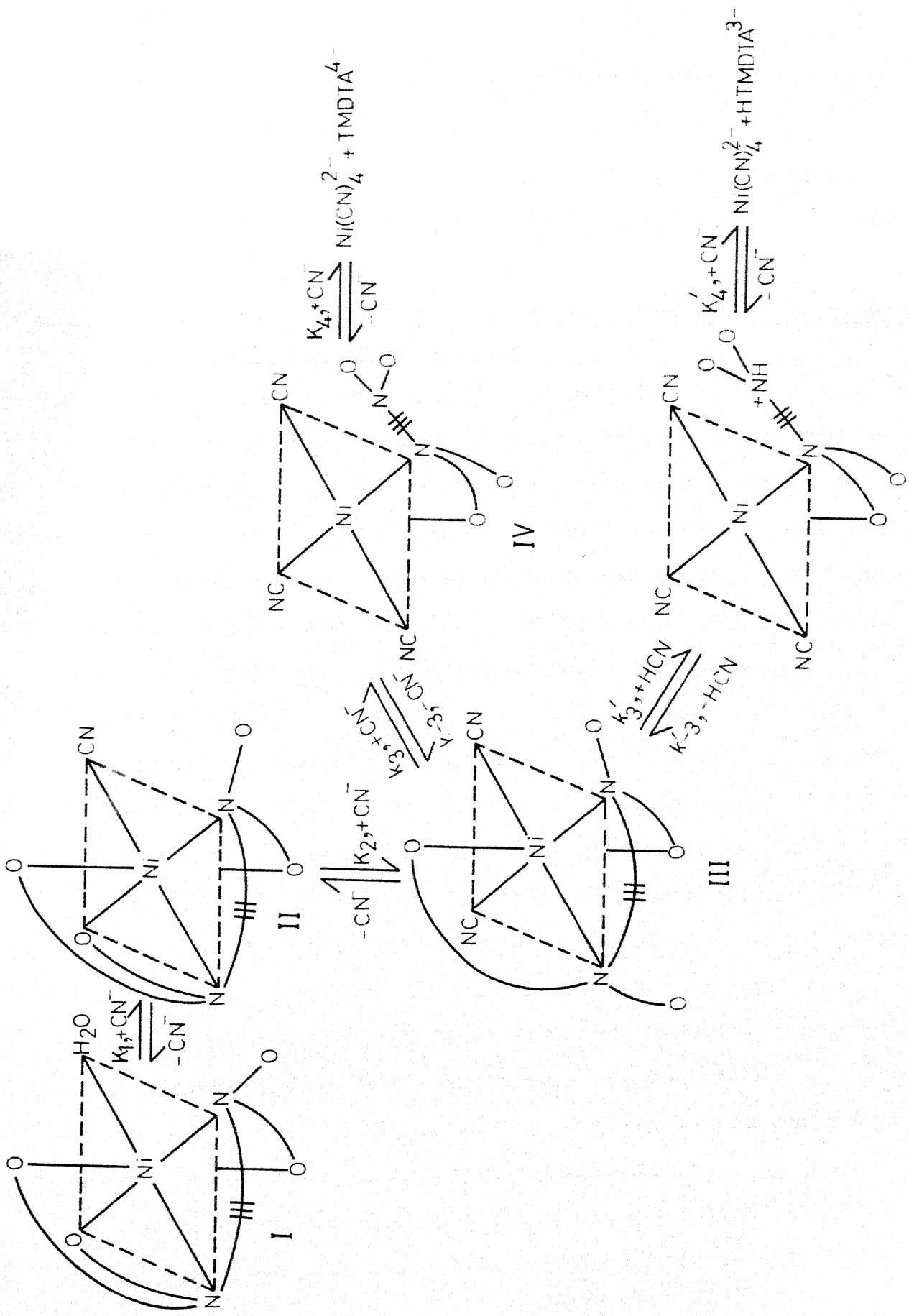


Fig. II.24 Stepwise Reaction Mechanism of Tetracyanonickelate(IV) Formation

reaction proceeds by an associative path⁷³ which is faster than the preceding steps as outlined in Figure II.24. The fourth cyanide adds very rapidly displacing the remaining glycinate segment of the ligand and finally producing diamagnetic $\text{Ni}(\text{CN})_4^{2-}$.

Determination of Stability Constants of Mixed Ligand Complexes by Kinetic and Mole Ratio Methods

An interesting off shoot of this work is that kinetic data obtained in the ligand substitution reactions can be used to determine the stability constants of mixed ligand complexes, $\text{NiL}(\text{CN})^{1-n}$ and $\text{NiL}(\text{CN})_2^{-n}$ formed in the first two steps of the four step mechanism. The reactions chosen for this study are TMDTA, 1,2-PDTA, DTPA and TTHA from this work and EDDA, NTA, HPDTA and EDTA reactions from previously published work.³⁻⁵ The values of stability constants of 1:1:1 complexes were also determined by the mole ratio method⁷⁴ in case of TMDTA, 1,2-PDTA, DTPA and TTHA. The stability constants of 1:1:2 complexes could not be determined by the mole ratio method in these cases because kinetic data show that these complexes exist only at higher cyanide concentration where the chances of formation of $\text{Ni}(\text{CN})_4^{2-}$ are certainly very much higher than for $\text{NiL}(\text{CN})_2$. $\text{Ni}(\text{CN})_4^{2-}$ formation from NiEDDA , NiNTA and NiHPDTA is very fast and had been investigated by stopped flow technique.³ In these cases also the stability constants of mixed ligand complexes cannot be verified by the mole ratio method.

It may be recalled that the forward reaction rate is first and second order in total cyanide concentration (always

taken in excess) in case of TMDTA, 1,2-PDTA, DTPA, TTHA and HPDTA, while first, second and third order dependence was observed for EDDA, NTA and HPDTA giving values of k_3 , K_2k_3 and $K_1K_2k_3$ respectively. The reverse rate constant $K_4^{-1}k_{-3}$ was evaluated from reverse rate studies in presence of excess L^{n-} . An expression that is useful where third order dependence is not observed experimentally has been derived in the earlier part of chapter (Eqn. 41) and reproduced below:

$$\frac{k_f}{k_r} = \frac{K_1K_2k_3}{K_4^{-1}k_{-3}} = \frac{\beta_4}{K_{NiL}}$$

The left hand side of this expression is the ratio of measured forward and reverse rate constants, k_f/k_r . Equation (41) enables one to calculate the value of $K_1K_2k_3$ from which one can calculate K_1 or K_1K_2 by knowing the experimental second and first order rate constants K_2k_3 and k_3 . These values are tabulated in Table II.16.

The stability constants of 1:1:3 complexes could not be evaluated because the reverse rate constants k_r ($= K_4^{-1} \cdot k_{-3}$) could not be resolved experimentally and k_{-3} could not be calculated.

The stability constants of the mixed ligand complexes have been defined earlier (Eqns. 7 and 8) and their values obtained by the kinetic data can be checked with the values determined independently by the mole ratio method.

Evaluation of Stability Constants of Mixed Ligand 1:1:1 Complexes by the Mole Ratio Method

The stability constants of these intermediate species involved in the formation of tetracyanonickelate(II) have been determined spectrophotometrically. The values of $\epsilon_{\text{NiL}(\text{CN})}$ for each complex have been determined (Table II.14) from absorption

Table II.14. λ_{max} and molar absorptivities of different mixed ligand complexes $\text{NiL}(\text{CN})^{1-n}$

System	λ_{max} , nm	$\epsilon_{\text{NiL}(\text{CN})}$, $\text{M}^{-1}\text{cm}^{-1}$
$\text{Ni}(\text{TMDTA})(\text{CN})^{3-}$	267	1.00×10^3
$\text{Ni}(1,2\text{-PDTA})(\text{CN})^{3-}$	255	1.36×10^3
$\text{Ni}(\text{DTPA})(\text{CN})^{4-}$	260	6.40×10^2
$\text{NiTTTHA}(\text{CN})^{5-}$	244	1.42×10^3

spectra of these complexes (Figure II.25) at their λ_{max} values by taking NiL in large excess compared to CN^- so that the formation of $\text{Ni}(\text{CN})_4^{2-}$ and other mixed ligand complexes is reduced to minimum and can be ignored.

The concentrations of $\text{NiL}(\text{CN})^{-n+1}$ were calculated from Equation (43):

$$[\text{NiL}(\text{CN})^{1-n}] = \frac{A - A_{\text{NiL}}}{b [\epsilon_{\text{NiL}(\text{CN})} - \epsilon_{\text{NiL}}]} \quad \dots (43)$$

where A and A_{NiL} are absorptions corresponding to complex concentration $\text{NiL}(\text{CN})$ and NiL respectively, b is the path length

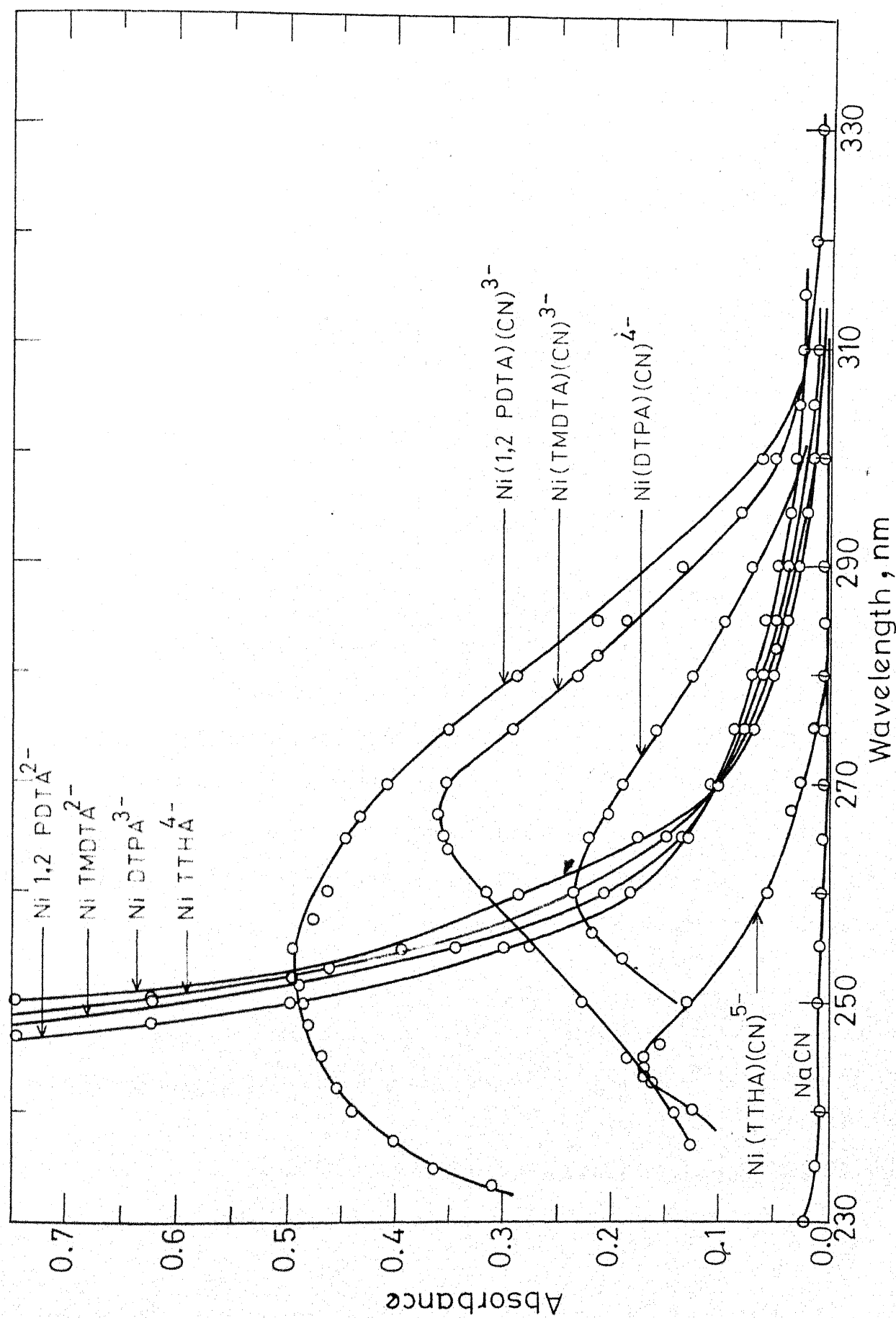


Fig. 11.25 Electronic Spectra of Mixed Ligand Complexes $\text{Ni}(\text{CN})$ where L is TMDTA, 1,2-PDPA, DTPA or TTHA, $[\text{Ni}, 1,2\text{-PDPA}(\text{CN})] = 3.60 \times 10^{-4} \text{ M}$, $[\text{Ni}, \text{TMDTA}(\text{CN})] = 3.6 \times 10^{-4} \text{ M}$, $[\text{Ni}, \text{DTPA}(\text{CN})] = 4.1 \times 10^{-4} \text{ M}$, $[\text{Ni}, \text{TTHA}(\text{CN})] = 1.26 \times 10^{-4} \text{ M}$

(1 cm) and ϵ 's are molar absorptivities of different $\text{NiL}(\text{CN})^{-n+1}$ and NiL^{-n+2} complexes respectively. Concentration of free NiL^{2-n} and CN^- were found by Equations (44) and (45). The subscript f denotes the equilibrium concentration of the species in question.

$$\begin{aligned} [\text{NiL}^{2-n}]_f &= [\text{NiL}^{2-n}]_T - [\text{NiL}(\text{CN})^{1-n}] \\ &= [\text{NiL}^{2-n}]_T - \frac{A_{\text{NiL}(\text{CN})}}{\epsilon_{\text{NiL}(\text{CN})}} \quad \dots (44) \end{aligned}$$

$$\begin{aligned} \text{and } [\text{CN}^-]_f &= [\text{CN}]_T - [\text{NiL}(\text{CN})^{1-n}] \\ &= [\text{CN}]_T - \frac{A_{\text{NiL}(\text{CN})}}{\epsilon_{\text{NiL}(\text{CN})}} \quad \dots (45) \end{aligned}$$

The stability constants K_{111} (or K_1) have been calculated by inserting appropriate concentration values in Equation (7). These values are given in Table II.15 and plots are shown in Figure II.26 and can be compared with those obtained from the kinetic method in Table II.16. The values of stability constants obtained by these two methods are in good agreement except in case of 1,2-PDTA which is due to the presence of methyl group in the branch chain of 1,2-PDTA which reduces the forward rate (see earlier discussion part).

This analysis shows that the kinetic method used herein is, in general, a reliable method for evaluation of stability constants of mixed ligand complexes produced in the intermediate steps of a multistep reaction. It can be used with advantage when the fast rate of formation of an end product, in this case

Table II.15. Determination of stability constants of 1:1:1 complexes of aminocarboxylate and cyanide with nickel(II)

$$t = 25 \pm 0.1^\circ \text{C}; \mu = 0.1 \text{ M (NaClO}_4\text{)}; [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M.}$$

$[\text{NiL}^{2-n}]_T$	$[\text{CN}^-]_T$	$[\text{NiL}(\text{CN})^{1-n}]$	$[\text{NiL}^{2-n}]_f$	$[\text{CN}^-]_f$	$K_{\text{NiL}(\text{CN})}$
<u>1. Ni(TMDTA)-(CN) Reaction System</u>					
3.4×10^{-4}	3.56×10^{-5}	2.95×10^{-5}	3.15×10^{-4}	6.10×10^{-6}	1.55×10^4
3.34×10^{-4}	1.05×10^{-4}	9.00×10^{-5}	2.44×10^{-4}	1.50×10^{-5}	2.50×10^4
3.19×10^{-4}	2.67×10^{-4}	2.00×10^{-4}	1.90×10^{-4}	6.70×10^{-5}	2.50×10^4
3.07×10^{-4}	3.86×10^{-4}	2.40×10^{-4}	6.70×10^{-5}	1.46×10^{-4}	2.45×10^4
2.99×10^{-4}	4.70×10^{-4}	2.50×10^{-4}	4.90×10^{-5}	2.20×10^{-4}	2.34×10^4
2.94×10^{-4}	5.23×10^{-4}	2.60×10^{-4}	3.40×10^{-5}	2.63×10^{-4}	2.90×10^4
2.87×10^{-4}	6.00×10^{-4}	2.60×10^{-4}	2.70×10^{-5}	3.30×10^{-4}	2.91×10^4
2.75×10^{-4}	7.20×10^{-4}	2.60×10^{-4}	1.50×10^{-5}	4.40×10^{-4}	2.90×10^4
					$\text{Av} = (2.50 \pm 0.3) \times 10^4$
<u>2. Ni(1,2-PDTA)-(CN) Reaction System</u>					
5.49×10^{-4}	7.06×10^{-5}	2.94×10^{-5}	5.20×10^{-4}	4.12×10^{-5}	1.37×10^3
5.44×10^{-4}	1.05×10^{-4}	3.82×10^{-5}	5.06×10^{-4}	6.68×10^{-5}	1.13×10^3
5.33×10^{-4}	1.71×10^{-4}	5.88×10^{-5}	4.74×10^{-4}	1.12×10^{-4}	1.11×10^3
5.23×10^{-4}	2.36×10^{-4}	7.72×10^{-5}	4.46×10^{-4}	1.59×10^{-4}	1.09×10^3
5.14×10^{-4}	2.97×10^{-4}	8.82×10^{-5}	4.26×10^{-4}	2.09×10^{-4}	0.99×10^3
5.10×10^{-4}	3.27×10^{-4}	1.07×10^{-4}	4.03×10^{-4}	2.20×10^{-4}	1.21×10^3
5.00×10^{-4}	3.86×10^{-4}	1.21×10^{-4}	3.79×10^{-4}	2.65×10^{-4}	1.21×10^3
4.87×10^{-4}	4.69×10^{-4}	1.36×10^{-4}	3.51×10^{-4}	3.33×10^{-4}	1.16×10^3
4.67×10^{-4}	6.00×10^{-4}	1.73×10^{-4}	2.94×10^{-4}	4.27×10^{-4}	1.37×10^3
4.48×10^{-4}	7.20×10^{-4}	1.88×10^{-4}	2.60×10^{-4}	5.32×10^{-4}	1.37×10^3
					$\text{Av} = (1.20 \pm 0.1) \times 10^3$

...contd.

Table II.15 (contd.)

3. Ni(DTPA)-(CN) Reaction System

1.00×10^{-3}	7.06×10^{-5}	1.09×10^{-5}	9.89×10^{-4}	5.97×10^{-5}	1.84×10^2
9.36×10^{-4}	2.97×10^{-4}	8.13×10^{-5}	8.55×10^{-4}	2.16×10^{-4}	4.36×10^2
9.19×10^{-4}	3.57×10^{-4}	8.90×10^{-5}	8.38×10^{-4}	2.68×10^{-4}	4.05×10^2
9.03×10^{-4}	4.14×10^{-4}	1.00×10^{-4}	8.03×10^{-4}	3.14×10^{-4}	4.00×10^2
8.87×10^{-4}	4.76×10^{-4}	1.09×10^{-4}	7.78×10^{-4}	3.70×10^{-4}	3.78×10^2
8.50×10^{-4}	6.00×10^{-4}	1.41×10^{-4}	7.44×10^{-4}	4.59×10^{-4}	4.19×10^2
8.16×10^{-4}	7.20×10^{-4}	1.61×10^{-4}	6.49×10^{-4}	5.53×10^{-4}	4.65×10^2
7.85×10^{-4}	8.30×10^{-4}	1.88×10^{-4}	5.97×10^{-4}	6.92×10^{-4}	4.91×10^2
7.56×10^{-4}	9.33×10^{-4}	2.11×10^{-4}	5.45×10^{-4}	7.22×10^{-4}	5.37×10^2
7.29×10^{-4}	1.03×10^{-4}	2.27×10^{-4}	5.02×10^{-4}	8.03×10^{-4}	5.63×10^2
7.03×10^{-4}	1.12×10^{-4}	2.30×10^{-4}	4.73×10^{-4}	8.90×10^{-4}	5.46×10^2
6.80×10^{-4}	1.20×10^{-4}	2.34×10^{-4}	4.46×10^{-4}	9.66×10^{-4}	5.53×10^2

$$Av = (4.40 \pm 0.5) \times 10^2$$

4. Ni(TTHA)-(CN) Reaction System

1.98×10^{-4}	2.37×10^{-5}	7.70×10^{-6}	1.90×10^{-4}	1.59×10^{-5}	2.57×10^3
1.96×10^{-4}	4.70×10^{-5}	1.06×10^{-5}	1.85×10^{-4}	3.64×10^{-5}	1.57×10^3
1.94×10^{-4}	6.99×10^{-5}	1.55×10^{-5}	1.79×10^{-4}	5.44×10^{-5}	1.59×10^3
1.92×10^{-4}	9.23×10^{-5}	1.55×10^{-5}	1.77×10^{-4}	7.67×10^{-5}	1.14×10^3
1.90×10^{-4}	1.14×10^{-4}	1.77×10^{-5}	1.72×10^{-4}	9.63×10^{-5}	1.06×10^3
1.86×10^{-4}	1.57×10^{-4}	1.91×10^{-5}	1.67×10^{-4}	1.38×10^{-4}	0.83×10^3
1.83×10^{-4}	1.98×10^{-4}	2.12×10^{-5}	1.62×10^{-4}	1.77×10^{-4}	0.74×10^3
1.81×10^{-4}	2.18×10^{-4}	2.47×10^{-5}	1.56×10^{-4}	1.93×10^{-4}	0.82×10^3

$$Av = (1.10 \pm 0.13) \times 10^3$$

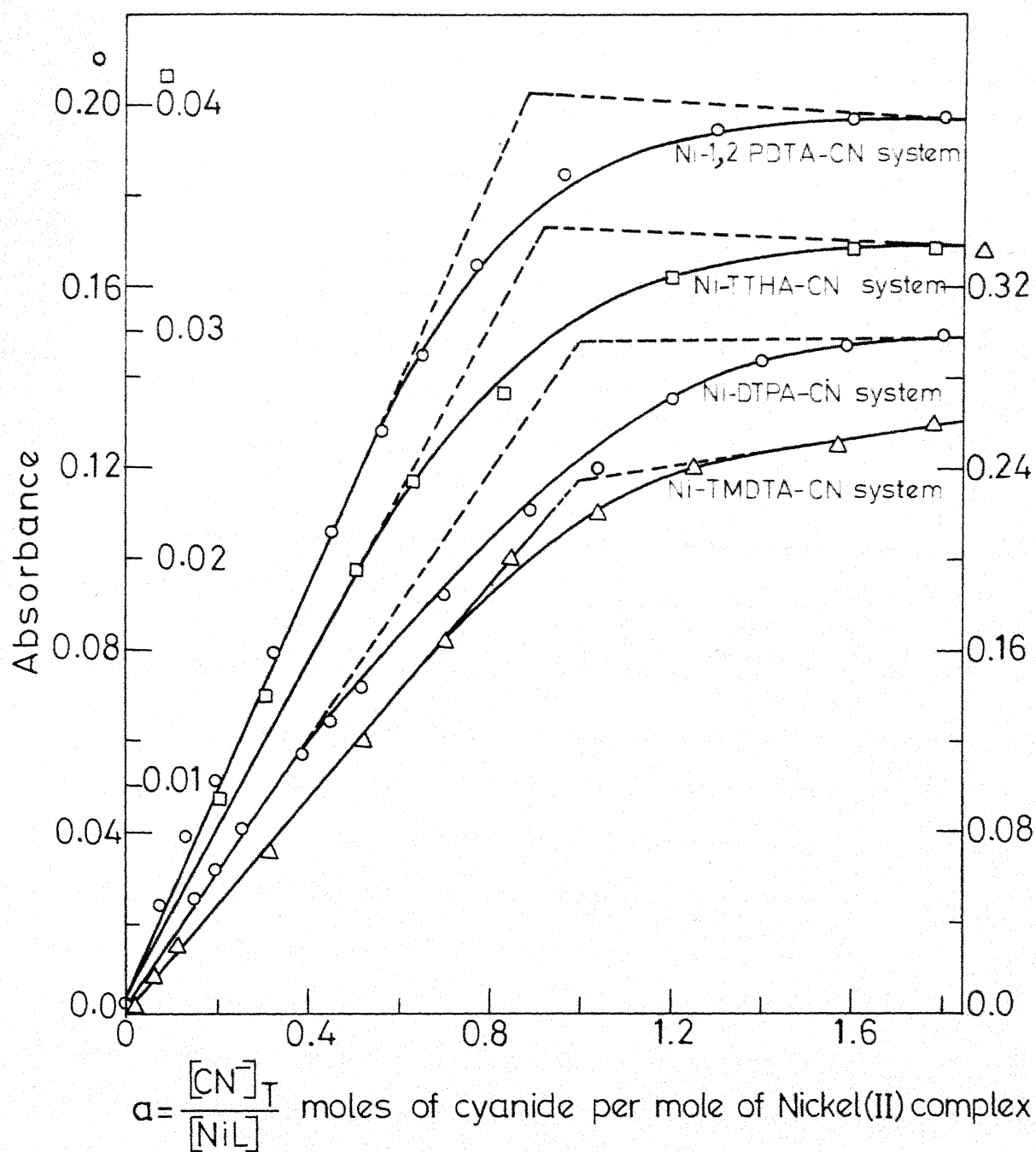


Fig. 11.26 Mole Ratio Plots for the Mixed Ligand Complexes $\text{NiL}(\text{CN})$ at temp = 25°C ; pH = 11.0 $\mu = 0.5 \text{ M}$

$\text{Ni}(\text{CN})_4^{2-}$, do not permit the application of conventional methods.

Table II.16. Stability constants of mixed ligand complexes
(log K values) by the kinetic & mole ratio methods

temp = $25 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ M}$ (NaClO_4); pH = 11.0 ± 0.2 .

System	K_{NiL}^*	K_{111} (or K_1)	K_2	β_{112}	K_{111} (or K_1) by mole ratio method
TMDTA	18.07	4.26	1.81	6.08	4.20
1,2-PDTA	19.6	4.06	0.49	4.55	3.08
DTPA	20.2	2.23	1.22	3.36	2.68
TTHA	18.2	3.08	2.95	6.03	3.04

*Taken from Table II.2.

Another interesting feature of this work is existence of a linear free energy relationship between stepwise rate constants k'_n (where $k'_1 = K_1 K_2 k_3$, the third order rate constant in cyanide; $k'_2 = K_2 k_3$, the second order rate constant in cyanide; and $k'_3 = k_3$ the first order rate constant in cyanide) and the respective overall stability constants of the reacting species viz., K_{NiL} , β_{111} of $\text{NiL}(\text{CN})$ and β_{112} of $\text{NiL}(\text{CN})_2$ respectively formed in the stepwise reaction of CN^- with NiL complexes. In all seven NiL complexes were chosen - four from this work and three from literature.³⁻⁵ The respective overall stability constants are defined in Equations (46 - 48):

$$K_{\text{NiL}} = \frac{[\text{NiL}]}{[\text{Ni}^{2+}][\text{L}^{n-}]} \quad \dots (46)$$

$$K_{\text{NiL}(\text{CN})} = \frac{[\text{NiL}(\text{CN})]}{[\text{NiL}][\text{CN}^-]} = \frac{[\text{NiL}(\text{CN})]}{K_1 [\text{Ni}^{2+}] [\text{L}^{n-}] [\text{CN}^-]}$$

$$\beta_{111} = K_{\text{NiL}} \cdot K_1 \quad \dots (47)$$

$$\text{Similarly } \beta_{112} = K_1 K_2 \cdot K_{\text{NiL}} \quad \dots (48)$$

In order to illustrate the proposed relationship following graphs have been plotted:

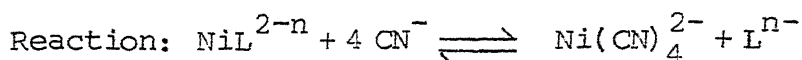
- $\log K_1 K_2 k_3$ versus $\log \beta_{110}$ ($\log K_1$),
- $\log K_2 k_3$ versus $\log \beta_{111}$,
- $\log k_3$ versus $\log \beta_{112}$.

These are shown in Figure II.27. The values of all these rate constants are chosen under identical conditions viz., temp = 25°C, μ = 0.1 M (NaClO_4), pH = 11.0 and are collected in Table II.17. Best fit straight lines have been obtained by the least square method. It is seen from Figure II.27 that the proposed relationship holds good generally. Two exceptions to this correlation viz., 1,2-PDTA and EDDA reactions have been explained in a recent publication.^{74a}

Interestingly, a linear relationship also exists between rate constants k'_n of an individual aminocarboxylatonickel(II) reaction with overall stability constant β_{1mn} of the intermediates NiL^{2-n} , $\text{NiL}(\text{CN})^{1-n}$ and $\text{NiL}(\text{CN})_2^{-n}$ of that particular reaction. The relationship is given in Equation (49):

$$\log k'_n = m' / \log \beta_{1mn} + C \quad \dots (49)$$

Table II.17. Rate constants, overall stability constants of each reacting species, slope (m) and intercept (c) of the equation



Reacting species	log of overall stability constants	Rate constants* k'_n	Slope m	Intercept	Ref.
1	2	3	4	5	6
<u>$\text{L}^{n-} : \text{EDDA}^{2-}$</u>					
NiL^{2-n}	13.50	$K_1 K_2 k_3 = 2.40 \times 10^{12}$	0.62	12.7	3
NiL(CN)^{1-n}	18.58	$K_2 k_3 = 2.10 \times 10^7$			
NiL(CN)_2^{-n}	21.68	$k_3 = 1.60 \times 10^4$			
<u>$\text{L}^{n-} : \text{NTA}^{3-}$</u>					
NiL^{2-n}	11.54	$K_1 K_2 k_3 = 1.00 \times 10^{11}$	0.63	14.4	3
NiL(CN)^{1-n}	16.26	$K_2 k_3 = 1.90 \times 10^6$			
NiL(CN)_2^{-n}	19.26	$k_3 = 2.00 \times 10^3$			
<u>$\text{L}^{n-} : \text{HPDTA}^{4-}$</u>					
NiL^{2-n}	16.45	$K_1 K_2 k_3 = 2.60 \times 10^6$	0.65	13.3	3
NiL(CN)^{1-n}	20.15	$K_2 k_3 = 5.07 \times 10^2$			
NiL(CN)_2^{-n}	22.63	$k_3 = 1.70$			
<u>$\text{L}^{n-} : 1, 2\text{-PDTA}^{4-}$</u>					
NiL^{2-n}	19.60	$K_1 K_2 k_3 = 1.90 \times 10^2$	0.60	13.9	29a
NiL(CN)^{1-n}	23.66	$K_2 k_3 = 1.77 \times 10^{-2}$			
NiL(CN)_2^{-n}	24.15	$k_3 = 5.70 \times 10^{-3}$			
<u>$\text{L}^{n-} : \text{TMDTA}^{4-}$</u>					
NiL^{2-n}	18.07	$K_1 K_2 k_3 = 5.27 \times 10^5$	0.60	12.5	30
NiL(CN)^{1-n}	22.34	$K_2 k_3 = 2.85 \times 10^5$			
NiL(CN)_2^{-n}	24.14	$k_3 = 4.38 \times 10^{-1}$			

..contd.

Table II.1 .(contd.)

1	2	3	4	5	6
<u>L^{n-}: DTPA⁵⁻</u>					
NiL^{2-n}	20.20	$K_1K_2k_3=7.50 \times 10^2$	0.64	13.7	29a
$NiL(CN)^{1-n}$	22.33	$K_2k_3=6.43$			
$NiL(CN)_2^{n-}$	23.56	$k_3=3.27 \times 10^{-1}$			
<u>L^{n-}: TTHA⁶⁻</u>					
NiL^{2-n}	18.80	$K_1K_2k_3=1.18 \times 10^5$	0.63	13.9	41
$NiL(CN)^{1-n}$	21.88	$K_2k_3=1.24 \times 10^2$			
$NiL(CN)_2^{n-}$	24.83	$k_3=1.47 \times 10^{-1}$			

*The units of rate constants are $K_1K_2k_3 = M^{-3}S^{-1}$; $K_2k_3 = M^{-2}S^{-1}$,
and $k_3 = M^{-1}S^{-1}$.

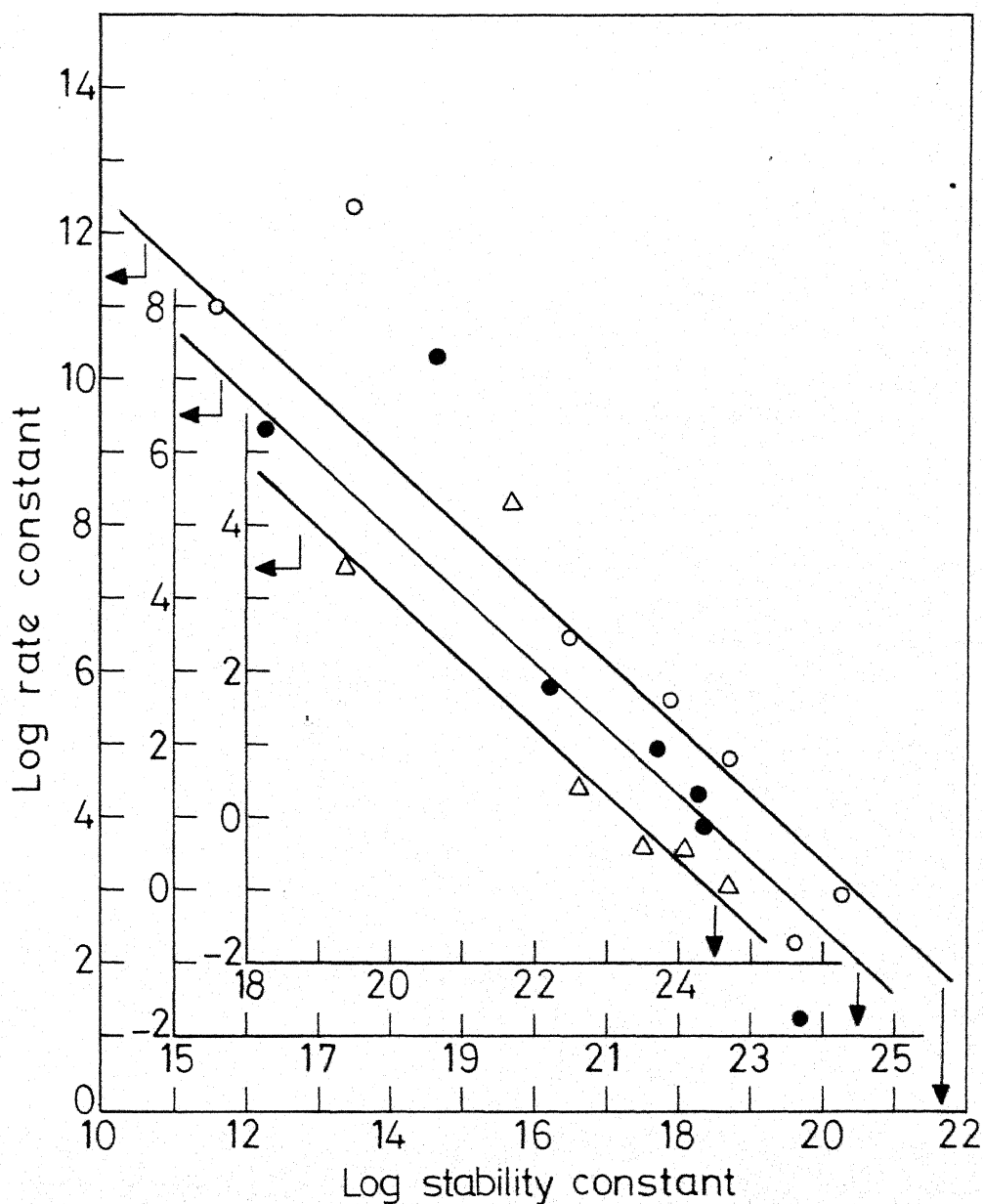


Fig. 11.27 Plots of log of Rate Constants ($K_1K_2k_3$, K_2k_3 or k_3) versus the log of Overall Stability Constants of the Reacting Species viz. NiL^{2-n} , $\text{NiL}(\text{CN})^{1-n}$ or $\text{NiL}(\text{CN})_2^{-n}$. O log of $K_1K_2k_3$ vs log K_{NiL} ; ● log K_2k_3 vs log β_{111} ; Δ log k_3 vs log β_{112}

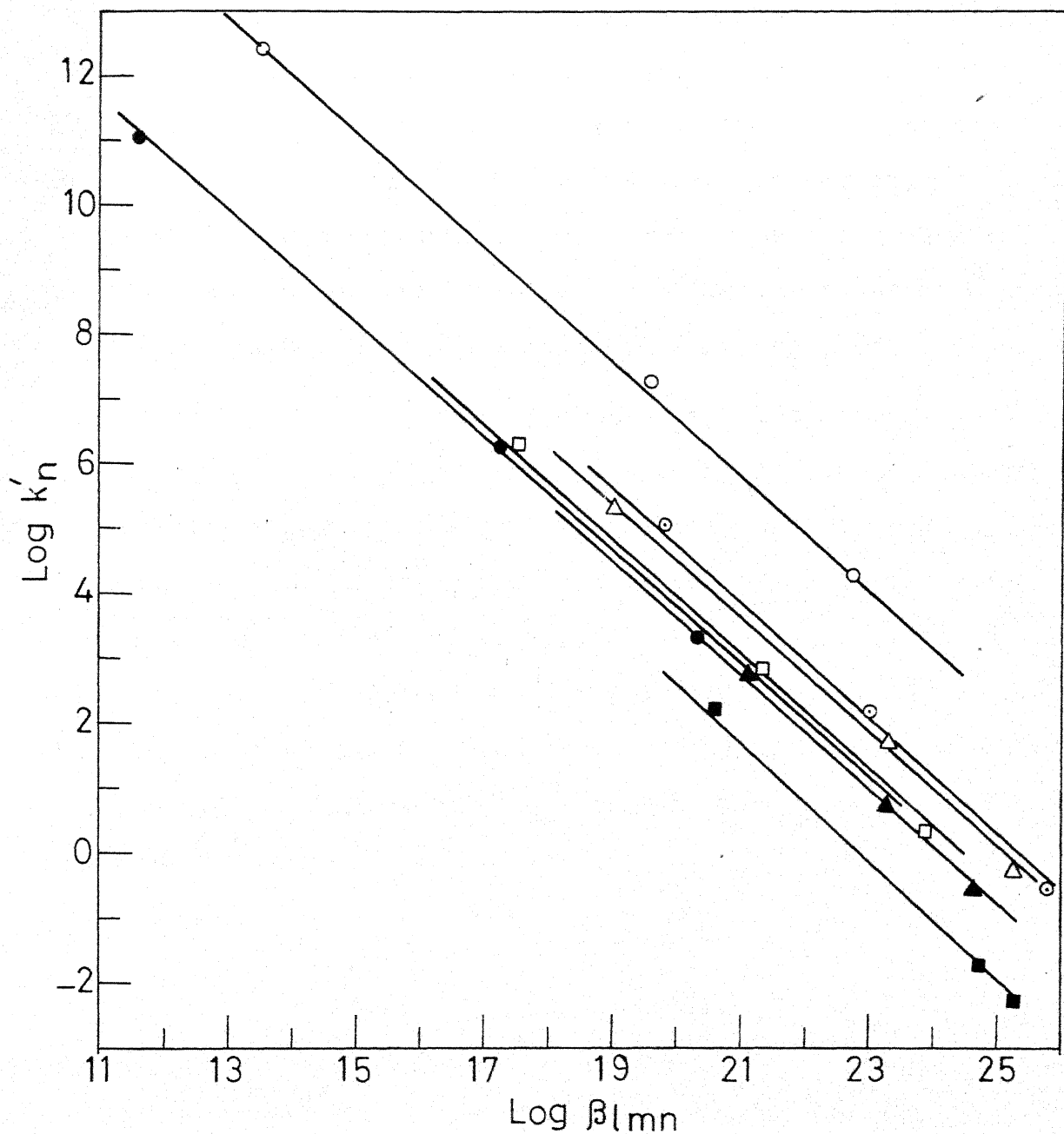


Fig. 11.28 Plot of $\log k'_n$ versus $\log \beta_{1mn}$. The different plots are for ○ EDDA; ● NTA; □ HPDTA; ■ 1,2-PDTA; △ TMDTA; ▲ DTPA; ⊙ TTHA.

where m' is the slope and C is a constant depending upon the system under investigation. The plots of equation (49) are given in Figure II.28. All straight lines have almost Equal slopes and slightly different intercepts. The near equality of all slopes appear to be due to the fact that all reactions follow the same mechanism; while the variation of intercept may be related to the structural peculiarities of NiL complexes. Not enough data is yet available to correlate the constant C with structural features of the individual NiL complexes or L itself.

Many LFERs have been proposed in the literature⁷⁵⁻⁷⁷ but the type of relationship discussed herein has not been proposed or verified experimentally so far. The novelty of the approach is that the rate constants for each step in the multistep reaction have been correlated to overall stability constants of reactive species involved in that particular step. This relationship enables one to calculate the overall stability constants of mixed complex intermediates from a knowledge of rate data or vice versa.

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CHAPTER III

MECHANISM OF TETRACYANONICKELATE FORMATION FROM BINUCLEAR NICKEL(II) COMPLEXES

ABSTRACT

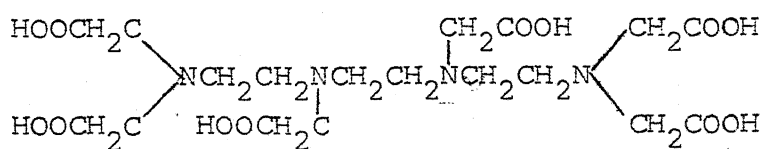
The mechanism of ligand substitution reactions of binuclear nickel(II) chelates Ni_2L , where L is $TTHA^{6-}$ (triethylenetetramine hexaacetic acid) and $DTPA^{5-}$ (diethylenetriamine pentaacetic acid) by cyanide ion has been investigated at $pH=11.0$, $\mu = 0.1$ M ($NaClO_4$) and $temp. = 25^\circ C$. The reaction is first order in Ni_2L and second and first order in cyanide in case of Ni_2TTHA and Ni_2DTPA respectively. At low concentrations of cyanides, however, both the reactions become zero order in cyanide. These results lead to a different mechanism than postulated by an earlier group of workers. Present results, including reinvestigation of their data, are interpreted to indicate the presence of slow dissociation of Ni_2L to NiL and $Ni^{2+}(aq)$ at low cyanide concentration and a cyanide assisted rapid dissociation to produce $NiL(CN)_x^{2-n-x}$ ($x = 1$ or 2) and $Ni^{2+}(aq)$ at higher cyanide concentration level. All these species react with excess

cyanide producing finally $\text{Ni}(\text{CN})_4^{2-}$. The formation of a mixed complex $\text{NiL}(\text{CN})$ in case of TTHA is verified spectrophotometrically. The pH dependence of forward reaction reveals that HCN is also a reactant between pH 7 to 9. Activation parameters for both reactions have been calculated.

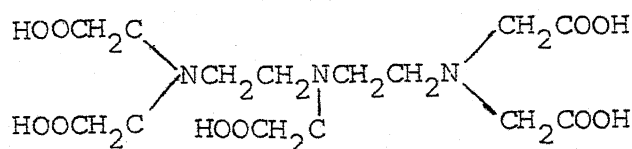
III.1 General

Triethylenetetramine hexaacetic acid (TTHA), and diethylenetriamine pentaacetic acid (DTPA), first introduced by Frost,¹ are multidentate ligands and both of them project multisites for coordination of metals. TTHA has ten while DTPA has eight binding sites.

The structures of these two ligands are given below:



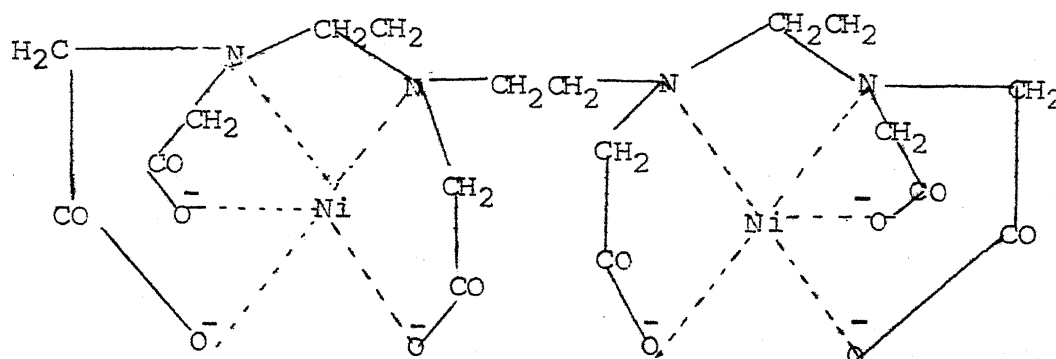
(I). TTHA



(II). DTPA

Potentiometric data obtained by Bohigian Jr. and Martell² for the 2:1 metal-ligand system for many metals indicated that

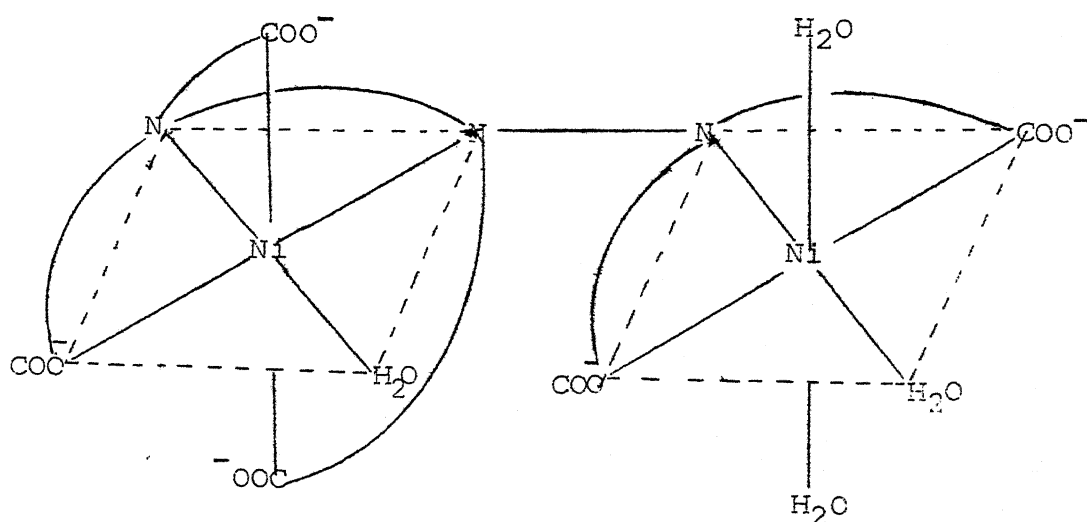
no protonated metal chelate species are formed in case of TTHA. Martell² has proposed a structure for the binuclear Cu^{2+} chelate. based on potentiometric studies. If it is assumed that the structure for nickel complex is similar to that of Cu^{2+} complex the structure of binuclear the former can be represented as given below (III):



III (Ni_2TTHA)

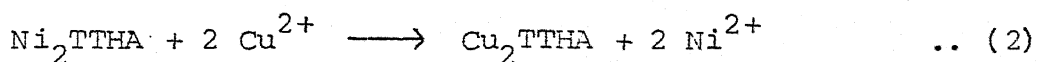
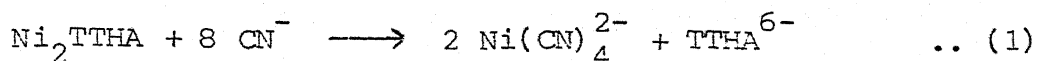
This structure is considered to be most probable since it depicts equal sharing of basic nitrogens and negative charges of ligand between the two metal ions in the complex.

Potentiometric titration data indicate that DTPA also forms a binuclear complex with nickel(II). The spectrum of binuclear nickel(II) DTPA complex exhibits only a single peak in carbonyl region indicating that uncoordinated carboxyl groups are absent. In view of this, a structural arrangement has been proposed by Bailar⁵ in which DTPA acts as a quinquidentate ligand toward one nickel ion, and is attached to the other nickel ion as a tridentate group as shown below (IV):

IV (Ni₂DTPA)

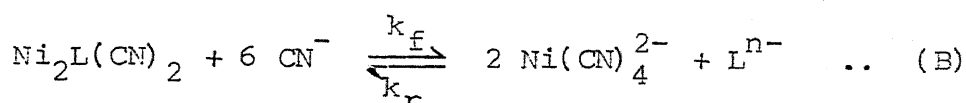
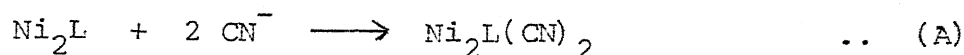
III.2 Introduction

The binuclear complexes of nickel(II) have attracted little attention in kinetic studies until recently, although rate data on binuclear complexes of Pt(II) have been reported in literature.⁶⁻¹⁷ Two reactions, involving binuclear complexes of Ni(II) both investigated by Stara and Kopanica,^{18a,b} which came to our notice are given in Equations (1) and (2):



A reinvestigation of the reaction of mononuclear complex viz., NiTTHA with cyanide^{19,20} led us to experimental findings and mechanism different from those reported by above workers¹⁸ but in line with one originally proposed by Margerum et al.²¹⁻²³ and confirmed by us^{24,25} and others.²⁶ In view of this

experience it was considered necessary to have a second look also at the reaction given in Equation (1) and our fears about their data and interpretation came to be true. According to these authors this reaction carried out in presence of large excess of CN^- , is first order in Ni_2L and second order in cyanide and follows a mechanism given in Equations (A) and (B):



But their explanation for this proposition is far from convincing. So reaction (1) was reinvestigated and another reaction between a second binuclear complex viz., Ni_2DTPA and CN^- was studied to confirm the findings.

In our investigation the reaction rate studies were extended to a much wider range of cyanide concentration than chosen by Stara and Kopanica¹⁸ and it was found, surprisingly, that the reaction becomes zero order in cyanide at concentration level lower than $1.0 \times 10^{-3} \text{ M}$. This indicates the dissociation of Ni_2L to NiL and $\text{Ni}^{2+}(\text{aquo})$. At higher cyanide concentration the order dependence in cyanide is two in case of Ni_2TTHA while it is one in case of Ni_2DTPA . The forward rate expression has a rate law of the form

$$\text{Rate} = \left\{ k_d + k_2' [\text{CN}]^x \right\} [\text{Ni}_2\text{L}] \quad \dots \text{ (3)}$$

where the values of rate constant k_d are relatively very small compared to that of k'_2 a constant corresponding to either a second order or a first order dependence in cyanide. These results coupled with a study of reverse reactions given in Chapter II lead us to a different mechanistic scheme than suggested by previous workers.¹⁸ The proposed scheme is discussed in a later section.

III.3 Experimental Section

The purified recrystallized varieties of TTHA and DTPA were obtained from Sigma Chemical Co., U.S.A. Microanalysis of C, H, and N at the Microanalytical Laboratory of I.I.T., Kanpur agreed very well with theoretical compositions of these ligands. Doubly distilled deionized water was used to prepare all the solutions.

A stock solution of nickel perchlorate obtained from Alpha Inorganics, U.S.A. was standardized against EDTA by complexometric titrations.²⁷

Sodium cyanide was obtained from M & B Ltd. Deganham, England. A stock solution of 1 M strength was prepared and standardized by titrating against AgNO_3 ²⁸ after suitable dilution each time before use.

The binuclear complexes of Ni(II) with TTHA and DTPA were prepared by adding a slight excess of nickel over stoichiometric amounts and removing excess nickel as Ni(OH)_2 at pH 10.0 by

milipore filtration through a $0.45\mu\text{m}$ filter. The solutions were allowed to stand in a cold room for two more days and finally filtered through a $0.22\mu\text{m}$ filter. The clear sparkling solutions were standardized by the addition of a large excess of NaCN at pH 11.0. After allowing for complete conversion to $\text{Ni}(\text{CN})_4^{2-}$ the absorbances were measured at 267 nm ($\epsilon = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and at 285 nm ($\epsilon = 4.63 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) using suitable dilutions.

Kinetic Runs

From the electronic spectra of Ni_2L (Figure III.1) one can see that Ni_2TTHA & Ni_2DTPA complexes absorb in visible region and their absorption peaks are at 380 & 595 nm; and 380 & 605 nm respectively (Fig.III.1). But the reaction product viz., $\text{Ni}(\text{CN})_4^{2-}$ gives sharp peaks at 267 and 285 nm. The reaction was monitored either at 267 nm or 285 nm by following the concentration of $\text{Ni}(\text{CN})_4^{2-}$ as a function of time. It was tested that at these wavelengths the Ni_2L and cyanide ion do not absorb appreciably.* A Toshniwal Spectrophotometer model RL-02 (Beckman DU type) was used for this study. For temperature maintenance an ultrathermostat type 2NBE (G.D.R.) was used. A Toshniwal pH meter and an Elico Digital pH meter were used for checking the pH of the solutions.

*All reactions were run in presence of large excess of cyanide. The observed first order rate constants were evaluated from the linear plots of $\log (A_\infty - A_t)$ versus time, where A_t is absorbance at time t .

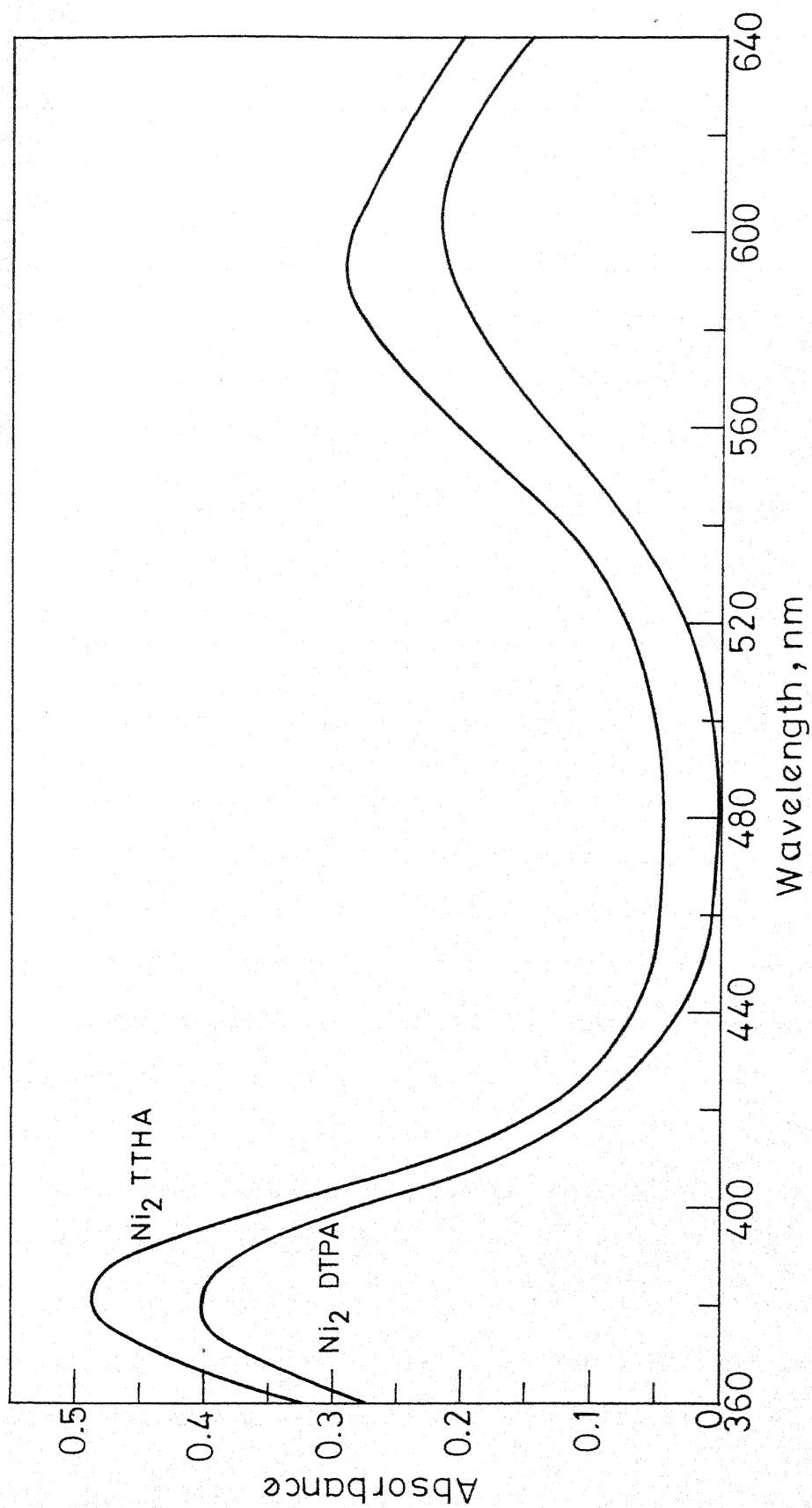


Fig. III.1 Absorption Spectra of $\text{Ni}_2 \text{TTHA}$ and $\text{Ni}_2 \text{DTPA}$ Complexes

III.4 Results

Kinetics of Reaction of Ni_2L with Cyanide

A computer calculation carried out by a program due to Perrin and Sayce,²⁹ as done in Chapter II, shows that starting with a metal to ligand ratio of 2:1 the binuclear complex was the only important chemical species in the working pH range (Fig. II.9 and Fig. II.10). Both reactions are thermodynamically favoured ($\log \beta_{Ni_2DTPA} = 25.70$,³⁰ $\log \beta_{Ni_2TTHA} = 32.2$,³¹ and $\log \beta_{4Ni(CN)_4} = 30.5$ ³²). The forward reactions were run in presence of excess cyanide under pseudo first order conditions. They were found to be first order in Ni_2L and first and second order in cyanide over a wide range of cyanide concentration in case of Ni_2DTPA and Ni_2TTHA respectively.

The observed pseudo-first order rate constants for Ni_2TTHA reaction at various levels of cyanide ion concentrations are given in Table III.1 and plotted in Fig. III.2 (k_{obsd} vs $[CN^-]_T$). A very significant feature is that the linear plots tend towards zero order dependence below 10^{-3} M cyanide concentration - an observation entirely ignored by Stara & Kopanica,^{18a} although their data also shows this trend (Fig. III.3). The same trend was confirmed in case of Ni_2DTPA reaction also, and the results are included in Table III.1 and Fig. III.2. The zero order dependence in cyanide indicates the dissociation of Ni_2L complexes according to Equation (4). It was also observed that when excess cyanide is added to either binuclear complex, there is

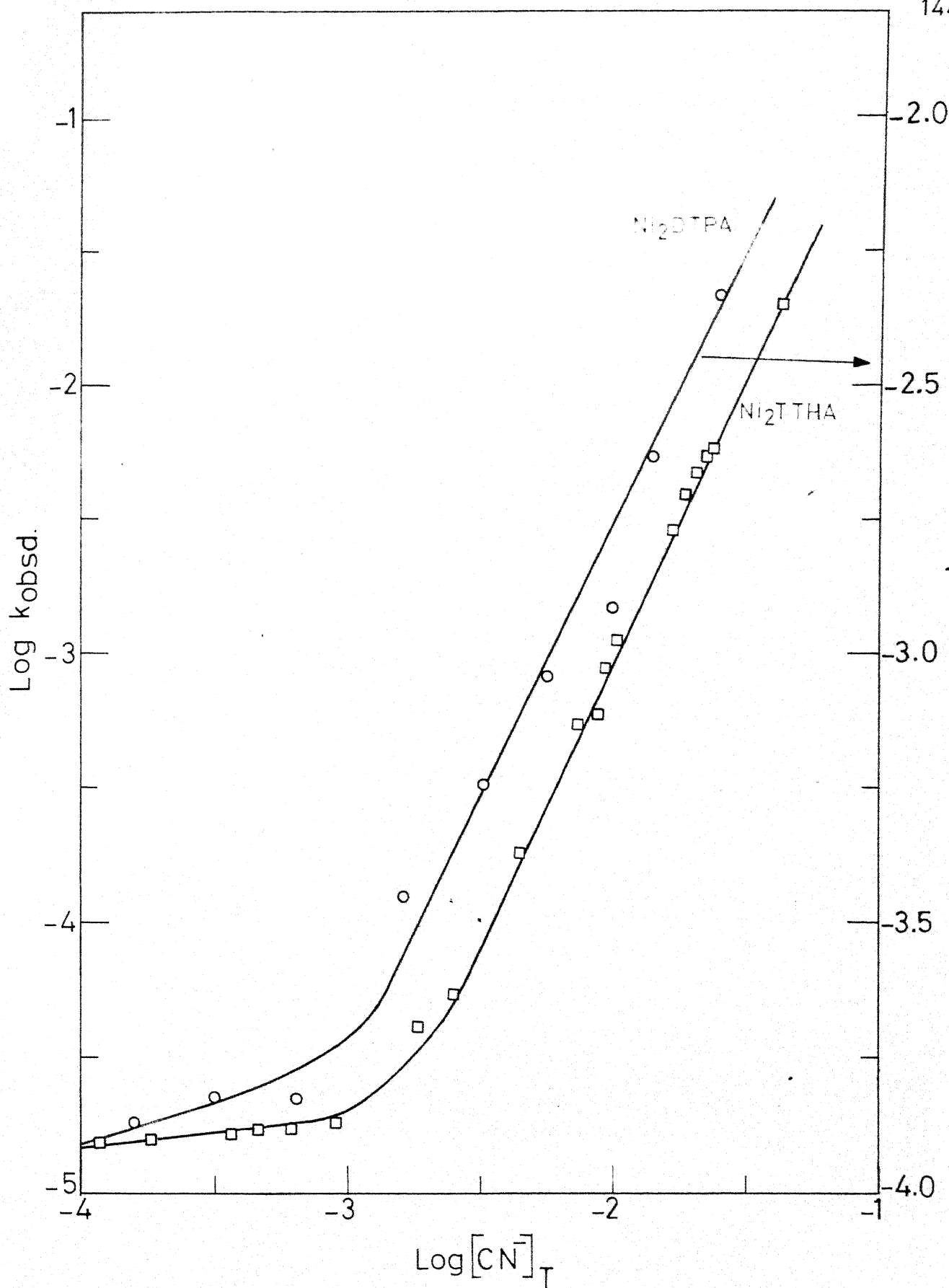


Fig. 111.2 Cyanide Dependence of the Observed Forward Rate

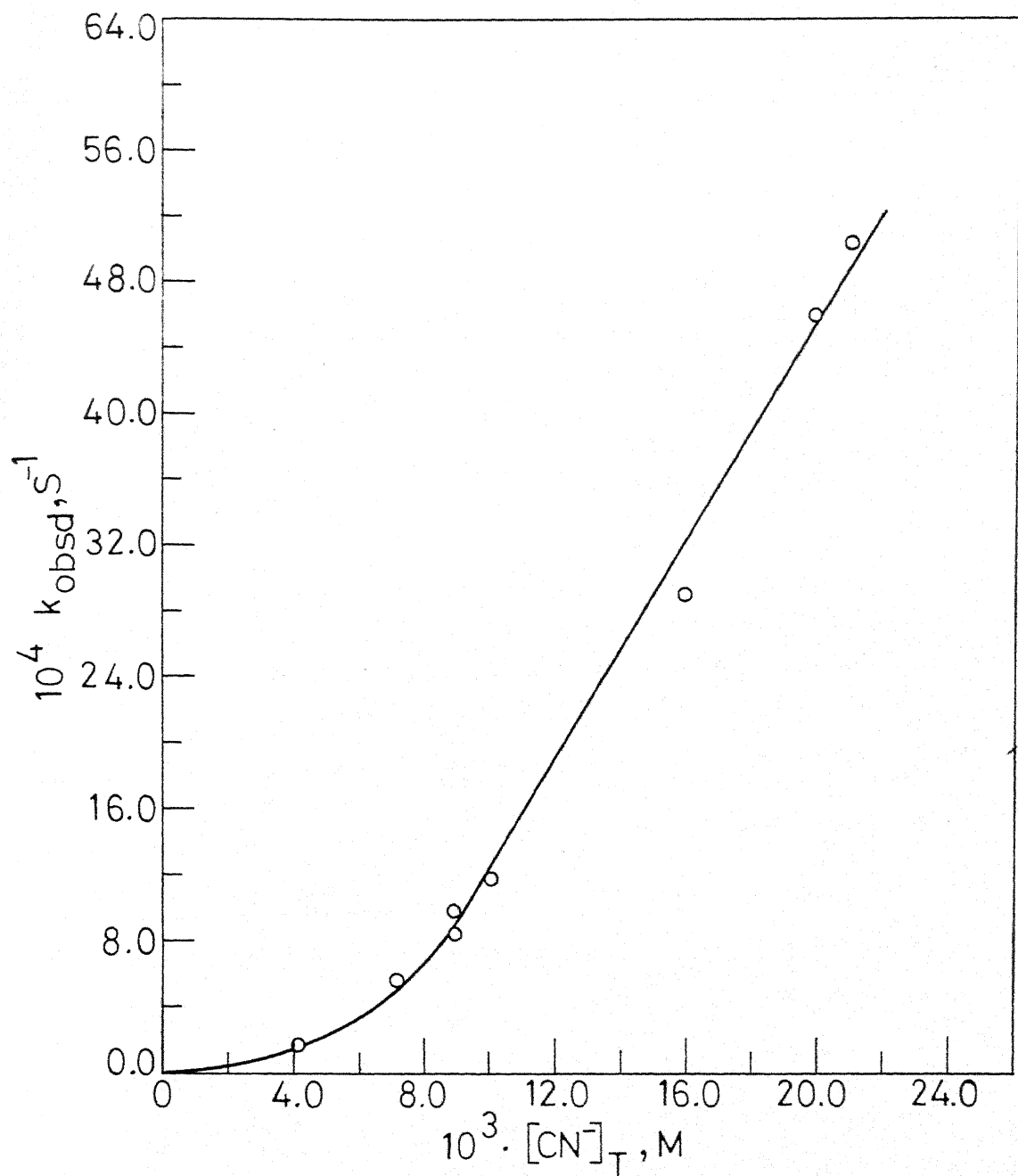
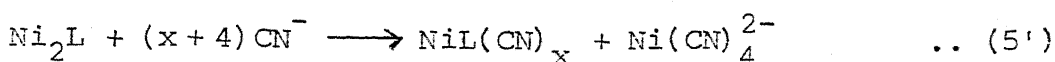
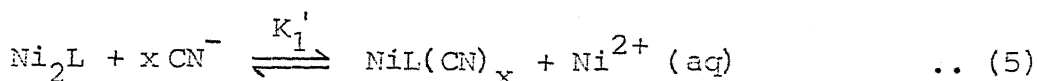
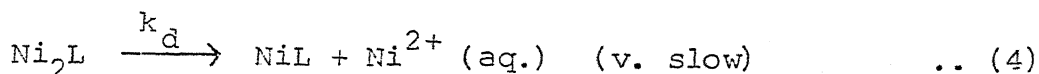


Fig. 111.3 Plot of k_{obsd} versus $[\text{CN}^-]_{\text{T}}$; data of Stara and Kopanica (Ref. Coll. Czech. Chem. Comm., 37, 2882 (1972))

an instantaneous and large absorbance change following mixing. This is due to cyanide assisted rapid dissociation of Ni_2L according to Equation (5) and the absorbance change is consistent with the net Equation (5'):



where L = TTHA or DTPA, $x = 2$ for TTHA and $x = 1$ for DTPA.

Table III.1. Rate constants for the reaction of Ni_2L^{2-} chelates with cyanide at temp = 25°C ; pH = 11.0; and $M = 0.1 \text{ M}$ (NaClO_4).

$[\text{CN}^-]_{\text{T}}, \text{M}$	$[\text{Ni}_2\text{L}], \text{M}$	$k_{\text{obsd}}, \text{s}^{-1}$
(i) $\text{Ni}_2\text{TTHA-CN}^-$ Reaction System		
1.13×10^{-4}	4.00×10^{-5}	$1.52 \times 10^{-5} \text{ (a)}$
1.80×10^{-4}	4.00×10^{-5}	$1.55 \times 10^{-5} \text{ (a)}$
2.25×10^{-4}	4.00×10^{-5}	$1.63 \times 10^{-5} \text{ (a)}$
4.50×10^{-4}	4.00×10^{-5}	$1.66 \times 10^{-5} \text{ (a)}$
6.00×10^{-4}	4.00×10^{-5}	$1.69 \times 10^{-5} \text{ (a)}$
9.00×10^{-4}	3.00×10^{-5}	$1.70 \times 10^{-5} \text{ (a)}$
1.80×10^{-3}	4.00×10^{-5}	4.51×10^{-5}
2.25×10^{-3}	4.20×10^{-5}	5.22×10^{-5}
4.20×10^{-3}	3.30×10^{-5}	1.86×10^{-4}

...contd.

Table III.1 (contd.)

4.50×10^{-3}	3.30×10^{-5}	1.90×10^{-4}
7.20×10^{-3}	1.50×10^{-4}	5.77×10^{-4}
9.00×10^{-3}	1.00×10^{-4}	9.61×10^{-4}
9.00×10^{-3}	5.00×10^{-4}	8.28×10^{-4}
1.02×10^{-2}	5.00×10^{-4}	1.10×10^{-3}
1.60×10^{-2}	1.00×10^{-4}	2.28×10^{-3}
1.60×10^{-2}	1.50×10^{-4}	2.28×10^{-3}
1.80×10^{-2}	4.20×10^{-5}	3.66×10^{-3}
2.00×10^{-2}	1.00×10^{-4}	4.61×10^{-3}
2.10×10^{-2}	5.00×10^{-4}	5.03×10^{-3}
2.25×10^{-2}	1.50×10^{-4}	5.68×10^{-3}
4.20×10^{-2}	5.00×10^{-4}	1.98×10^{-2}

(ii) $\text{Ni}_2\text{DTPA-CN}^-$ Reaction System

1.55×10^{-4}	4.39×10^{-5}	$1.34 \times 10^{-4} \text{ (a)}$
3.10×10^{-4}	5.25×10^{-5}	$1.53 \times 10^{-4} \text{ (a)}$
6.20×10^{-4}	3.96×10^{-5}	$1.35 \times 10^{-4} \text{ (a)}$
7.75×10^{-4}	3.90×10^{-5}	$1.40 \times 10^{-4} \text{ (a)}$
1.55×10^{-3}	9.48×10^{-5}	3.69×10^{-4}
3.10×10^{-3}	9.30×10^{-5}	5.41×10^{-4}
6.20×10^{-3}	9.50×10^{-5}	7.96×10^{-4}
1.24×10^{-2}	6.20×10^{-5}	1.15×10^{-3}
1.50×10^{-2}	7.90×10^{-5}	2.20×10^{-3}
2.48×10^{-4}	7.41×10^{-5}	4.70×10^{-3}

(a) zero order rate constants in cyanide.

The NiL , $\text{NiL}(\text{CN})_x$ (where x is 1 or 2) and Ni^{2+} (aquo) produced in these steps react with excess cyanide forming $\text{Ni}(\text{CN})_4^{2-}$ finally. It was reported in our earlier communications^{20, 24} that when a small amount of cyanide was mixed to a tenfold excess of Ni_2L , mixed ligand complexes of $\text{NiL}(\text{CN})_x^{2-n-x}$ type form. In case of Ni_2TTHA a characteristic peak of $\text{NiL}(\text{CN})$ is ~~observed~~ spotted. A similar peak could not be seen in case of Ni_2DTPA reaction though it is apparent from the order dependence in cyanide that $\text{NiL}(\text{CN})_2$ is forming rapidly. No formation of Ni^{2+} (aquo) was detectable from dissociation of Ni_2L according to Eqn. (4). No precipitation or even colour change was seen when dimethylglyoxime was added to Ni_2L alone even on long standing but the same is obtained in presence of small amounts of cyanide. It is inferred from these experiments that in presence of CN^- the Ni_2L complex gives $\text{NiL}(\text{CN})_x$ and Ni^{2+} (aquo) according to Eqn. (5) and cyanide assists this decomposition. The subsequent steps are the same which have been postulated for the reactions of mono(aminocarboxylato) $\text{Ni}(\text{II})$ complexes with cyanide.¹⁹⁻²⁵

The reverse reaction in both cases are the same as for mononuclear complexes and relevant rate data have been given in Chapter II (Table II.4). There is no evidence for formation of Ni_2L in the reverse reaction.

Temperature Dependence of $\text{Ni}_2\text{L}-\text{CN}^-$ Reaction

The temperature dependence of the above two reactions was investigated over a temperature range of 25-40°C. The reaction

rates were found to obey the Arrhenius equation. The activation parameters have been calculated for both the situations where order dependences are zero and one or two respectively. These data are compiled in Table III.2 and plotted in Fig. III.4. The data have been used in support of postulated mechanism (vide supra). Activation parameters for reverse reactions have been determined and reported in Chapter II, Table II.6.

pH Dependence of $\text{Ni}_2\text{L-CN}^-$ Reaction

The pH dependence of the reactions was investigated in the pH range 7.5 - 11.5 under conditions where cyanide order dependence is two in case of $\text{Ni}_2\text{TTHA}^{2-}$ and one in case of $\text{Ni}_2\text{DTPA}^{1-}$. The data for both reactions are presented in Table III.3. The plots of $\log k_f$ versus $-\log [\text{H}^+]$ are given in Fig. III.5 ($k_f = k_{\text{obsd}} / [\text{CN}^-]^x$; $x = 1$ or 2). Like (mono) aminocarboxylato nickel(II) complex reactions, the k_f decreases as $[\text{H}^+]$ increases which is due to conversion of CN^- into a poorer nucleophile HCN . The slope of this plot is found to be one. A slope of two is expected in case of Ni_2TTHA if HCN were not a reactant. It is concluded that one molecule of HCN , one cyanide ion and $\text{Ni}(\text{TTHA})(\text{CN})$ are the reactants in the low pH range prior to the rate determining step. A rate expression valid for this pH range and cyanide concentration levels is

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = \{k_f [\text{CN}^-]^2 + k'_f [\text{CN}^-] [\text{HCN}]\} [\text{NiL}(\text{CN})] \quad \dots (6)$$

Table III.2. Temperature effect on the reaction of cyanide with binuclear aminocarboxylato nickel(II) complexes at pH = 11.0 \pm 0.1 and μ = 0.1 M (NaClO₄)

Temp. \pm 0.1°C	$k_{\text{obsd}}, \text{S}^{-1}$	Activation Parameters
(i) $\text{Ni}_2\text{TTHA-CN}^-$ Reaction System		
$[\text{Ni}_2\text{L}] = 4.30 \times 10^{-5} \text{ M}; [\text{CN}^-]_{\text{T}} = 6.20 \times 10^{-4} \text{ M}$ (zero order dependence)		
25	1.50×10^{-5}	E_a kcal; 14.8
30	2.02×10^{-5}	$\Delta H^{\circ\neq}$ kcal; 14.21
35	3.00×10^{-5}	$\Delta S^{\circ\neq}$, e.u.; -61.15
40	4.00×10^{-5}	pZ cm^{-1} ; 4.32×10^5
$[\text{Ni}_2\text{L}] = 6.20 \times 10^{-5} \text{ M}, [\text{CN}^-]_{\text{T}} = 9.0 \times 10^{-3} \text{ M}$ (second order dependence)		
25	1.10×10^{-3}	E_a kcal; 6.3
30	1.40×10^{-3}	$\Delta H^{\circ\neq}$ kcal; 5.71
35	1.62×10^{-3}	$\Delta S^{\circ\neq}$ e.u.; -34.0
40	1.91×10^{-3}	pZ cm^{-1} ; 4.32×10^5
(ii) $\text{Ni}_2\text{DTPA-CN}^-$ Reaction System		
$[\text{Ni}_2\text{L}] = 6.50 \times 10^{-5} \text{ M}; [\text{CN}^-]_{\text{T}} = 6.20 \times 10^{-4} \text{ M}$ (zero order dependence)		
25	1.35×10^{-4}	E_a kcal; 15.9
30	2.24×10^{-4}	$\Delta H^{\circ\neq}$ kcal; 15.31
40	5.01×10^{-4}	$\Delta S^{\circ\neq}$ e.u.; -24.59
45	7.20×10^{-4}	pZ cm^{-1} ; 2.51×10^7
$[\text{Ni}_2\text{L}] = 6.50 \times 10^{-5} \text{ M}; [\text{CN}^-]_{\text{T}} = 3.10 \times 10^{-3} \text{ M}$ (first order dependence)		
25	5.41×10^{-4}	E_a kcal; 5.2
35	7.57×10^{-4}	$\Delta H^{\circ\neq}$ kcal; 4.61
40	8.60×10^{-4}	$\Delta S^{\circ\neq}$, e.u.; -46.37
45	9.90×10^{-4}	pZ cm^{-1} ; 4.2×10^2

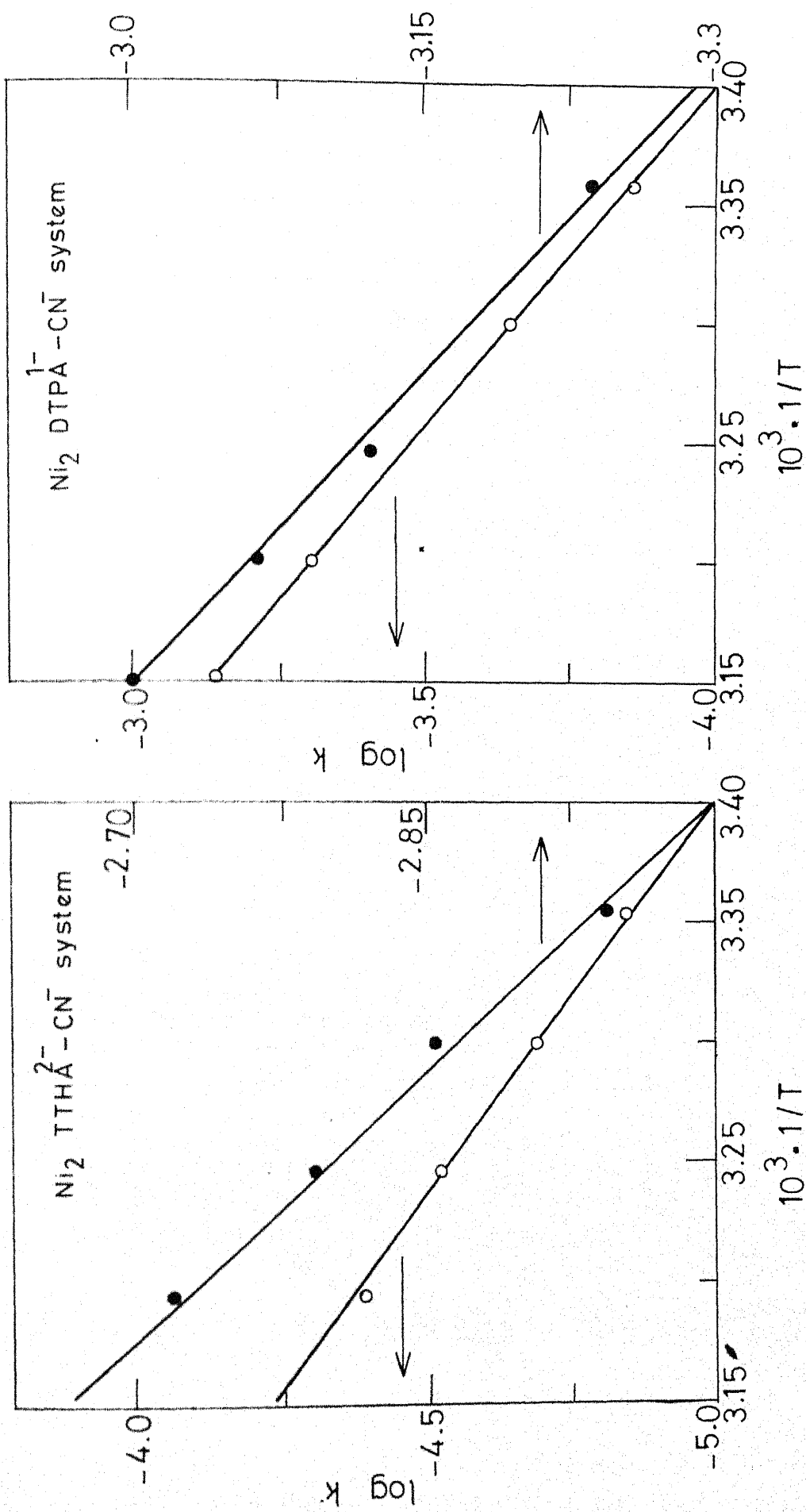


Fig. III.4 Effect of Temperature on the Reaction of Cyanide with Ni_2L ; Zero Order Dependence ●, First or Second order Dependence ○.

Table III.3. pH dependence of tetracyanonickelate(II) formation from binuclear aminocarboxylato nickel(II) complexes.

temp = $25 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ M (NaClO}_4\text{)}$

$-\log [\text{H}^+]$	$k_{\text{obsd}}, \text{ s}^{-1}$	$k_f = \frac{k_{\text{obsd}}}{[\text{CN}^-]^x}$
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(i) $\text{Ni}_2\text{TTHA-CN}^-$ Reaction System

$$[\text{Ni}_2\text{TTHA}^{2-}] = 5.80 \times 10^{-5} \text{ M}, [\text{CN}^-]_{\text{T}} = 9.0 \times 10^{-3} \text{ M}$$

6.9	9.60×10^{-7}	0.01
7.2	1.71×10^{-6}	0.02
8.1	1.93×10^{-5}	0.24
8.6	7.44×10^{-5}	0.87
8.9	1.69×10^{-4}	2.09
9.1	2.45×10^{-4}	3.03
9.4	5.21×10^{-4}	6.43
9.6	6.85×10^{-4}	8.47
9.9	8.02×10^{-4}	9.90
10.0	8.22×10^{-4}	10.15
10.9	8.20×10^{-4}	10.12

(ii) $\text{Ni}_2\text{DTPA-CN}^-$ Reaction System

$$[\text{Ni}_2\text{DTPA}] = 3.02 \times 10^{-5} \text{ M}, [\text{CN}^-]_{\text{T}} = 3.10 \times 10^{-3} \text{ M}$$

7.4	6.18×10^{-5}	0.02
7.9	3.11×10^{-4}	0.10
8.4	4.51×10^{-4}	0.15
8.9	6.77×10^{-4}	0.22
9.4	7.04×10^{-4}	0.22
9.9	7.10×10^{-4}	0.23
10.4	7.50×10^{-4}	0.24
10.9	8.30×10^{-4}	0.27

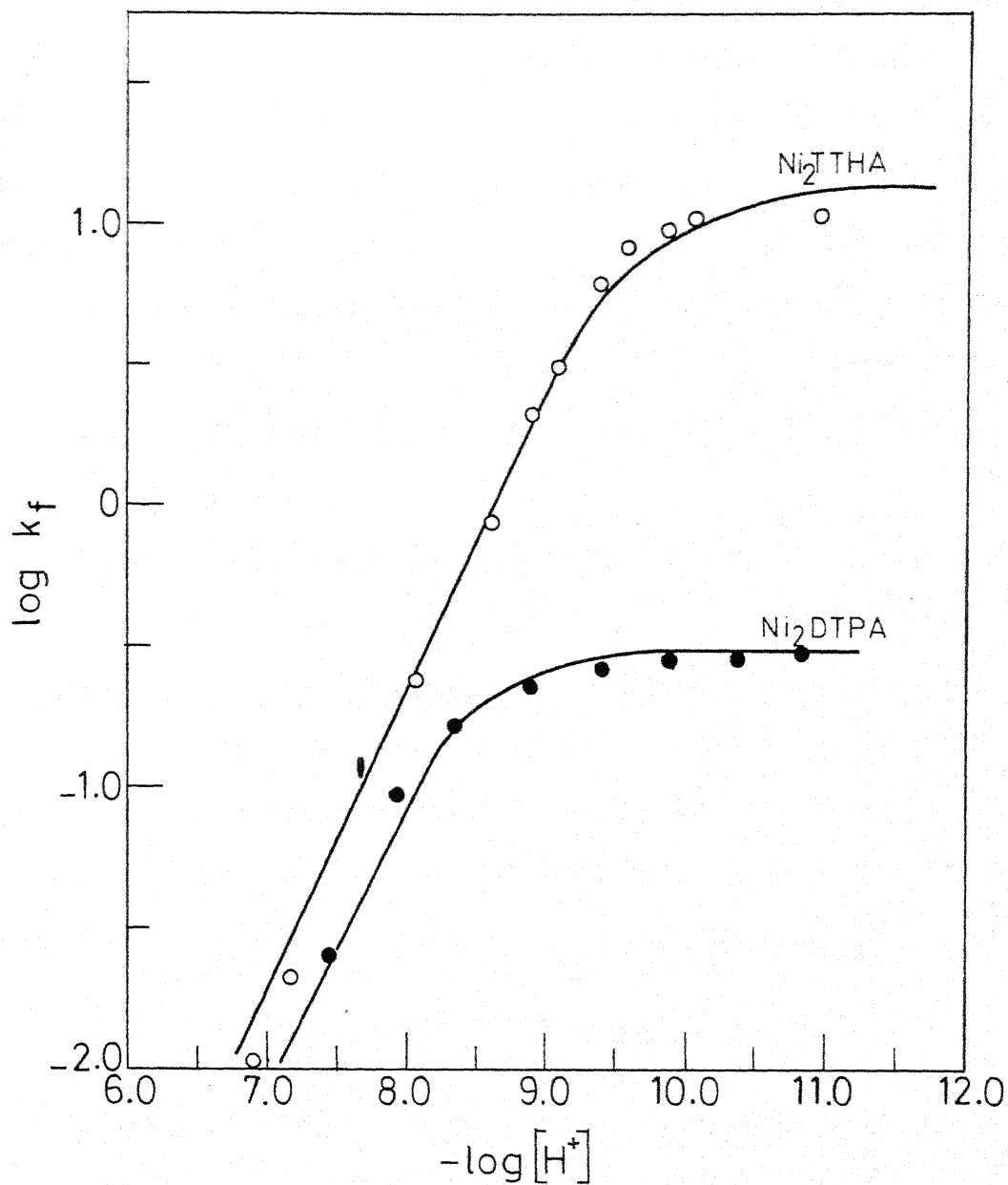


Fig. III.5 Effect of pH on the Reaction of Cyanide with Ni_2L

The pH dependence in case of Ni_2DTPA cyanide reaction is handled in a different manner. k_f the forward rate constant for this reaction decreases as pH decreases because a larger fraction of total cyanide is present as HCN. A function α_{CN} is defined as $\alpha_{\text{CN}} = K_a / ([\text{H}^+] + K_a)$, where K_a is the dissociation constant of HCN. When $k_f / [\text{CN}^-]$ is plotted against α_{CN} a straight line is obtained (Fig. III.6). This shows that two cyanides are involved in the reaction and the third cyanide must then add in the form of HCN. The rate expression for $\text{Ni}_2\text{DTPA-CN}^-$ reaction should take the form

$$\frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = \{k_f[\text{CN}^-] + k'_f[\text{HCN}]\}[\text{NiL}(\text{CN})_2] \quad \dots (6a)$$

Resolution of Rate Constants

The resolution of rate constants for Ni_2TTHA -cyanide reaction was done as described for (mono) aminocarboxylato $\text{Ni}(\text{II})$ exchange reactions in Chapter II. But for Ni_2DTPA reaction it was done as follows:

$$k_f[\text{CN}^-]_T = k_{f(\text{CN}^-)}[\text{CN}^-] + k_{f(\text{HCN})}[\text{HCN}] \quad \dots (7)$$

$$k_f \{[\text{CN}^-] + [\text{HCN}]\} = k_{f(\text{CN}^-)}[\text{CN}^-] + k_{f(\text{HCN})}[\text{HCN}]$$

$$k_f \left\{ [\text{CN}^-] + K_{\text{HCN}}[\text{H}^+][\text{CN}^-] \right\} = k_{f(\text{CN}^-)}[\text{CN}^-] + k_{f(\text{HCN})} \cdot K_{\text{HCN}} \cdot \frac{[\text{H}^+]}{[\text{CN}^-]}$$

$$k_f = \frac{k_{f(\text{CN}^-)} + k_{f(\text{HCN})} \cdot K_{\text{HCN}} \cdot [\text{H}^+]}{1 + K_{\text{HCN}}[\text{H}^+]} \quad \dots (8)$$

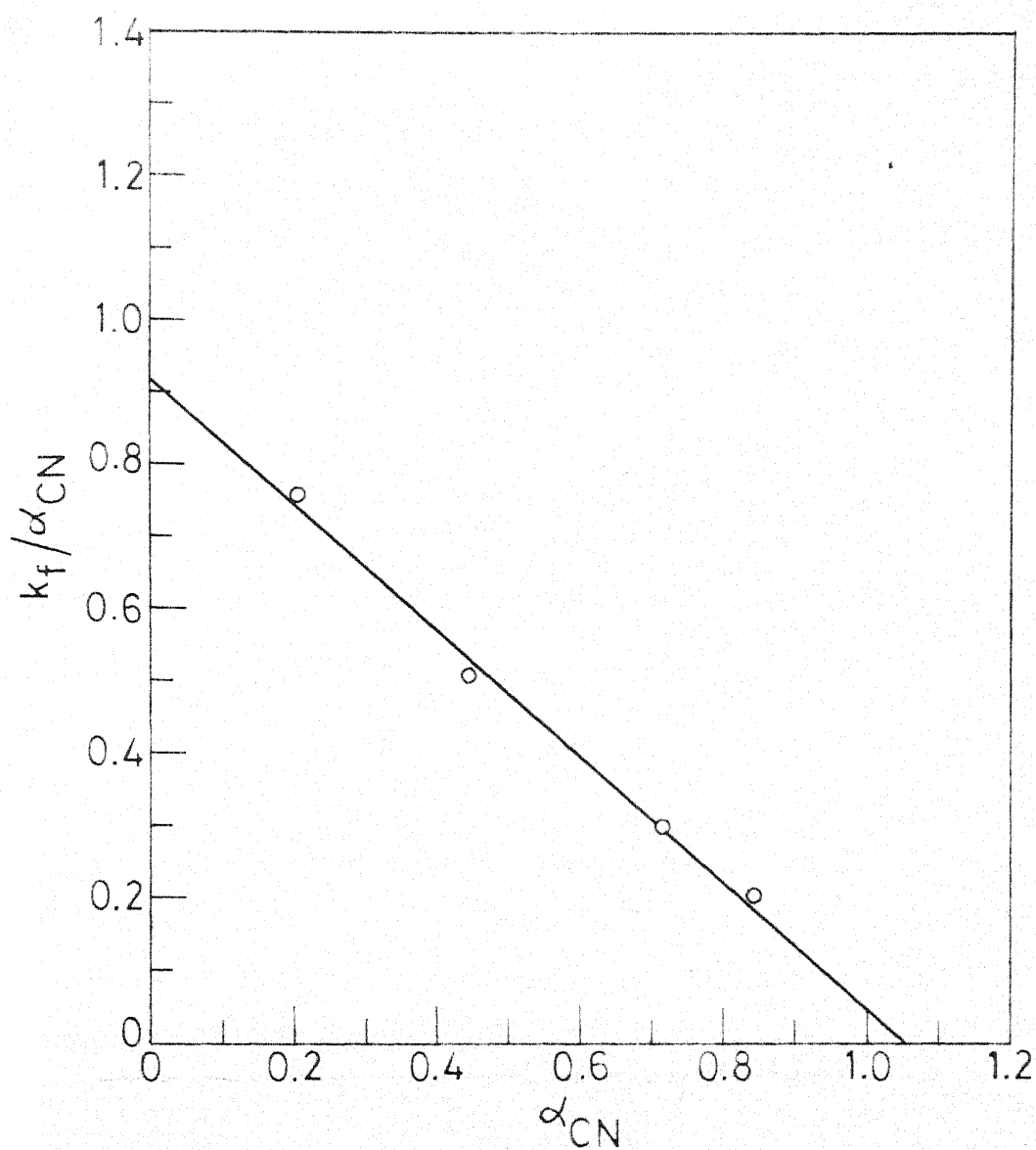


Fig. 11.6 Determination of Order in HCN for Ni_2DTPA System. Plot of k_f/α_{CN} versus α_{CN} , where $\alpha_{\text{CN}} = K_a/([H^+] + K_a)$ & K_a is the dissociation constant of HCN

where K_{HCN} is the protonation constant for CN^- . At higher pH $K_{\text{HCN}}[\text{H}^+]$ is negligible in comparison to 1 and the expression (8) takes the form

$$k_f = k_{f(\text{CN})} \quad \dots (9)$$

But below pH 9, one is negligible in comparison to the terms in the denominator and Equation (8) reduces to

$$k_f = \frac{k_{f(\text{CN})}}{K_{\text{HCN}}} \cdot 1/[\text{H}^+] + k_{f(\text{HCN})} \quad \dots (10)$$

A plot of k_f versus $1/[\text{H}^+]$ is shown in the Fig. III.7. The slope of straight line gives $k_{f(\text{CN})}$ while the intercept gives $k_{f(\text{HCN})}$. The values of $k_{f(\text{CN})}$ and $k_{f(\text{HCN})}$ for Ni_2DTPA reaction are $1.77 \times 10^{-1} \text{ M}^{-1}\text{S}^{-1}$ and $0.86 \times 10^{-1} \text{ M}^{-1}\text{S}^{-1}$ respectively. The corresponding values for Ni_2TTHA reaction calculated by the method discussed in Chapter II (Equation 21) are $10.15 \text{ M}^{-1}\text{S}^{-1}$ and $2.4 \text{ M}^{-2}\text{S}^{-1}$ respectively.

III.5 Discussion

On the basis of experimental observations it may be inferred that the initial part of the forward reaction seems to proceed by two paths, first a slow dissociation according to Equation (11) and a fast cyanide assisted dissociation according to Equation (12). These are followed by steps (13) to (15), Equation (14) being the rate determining step:

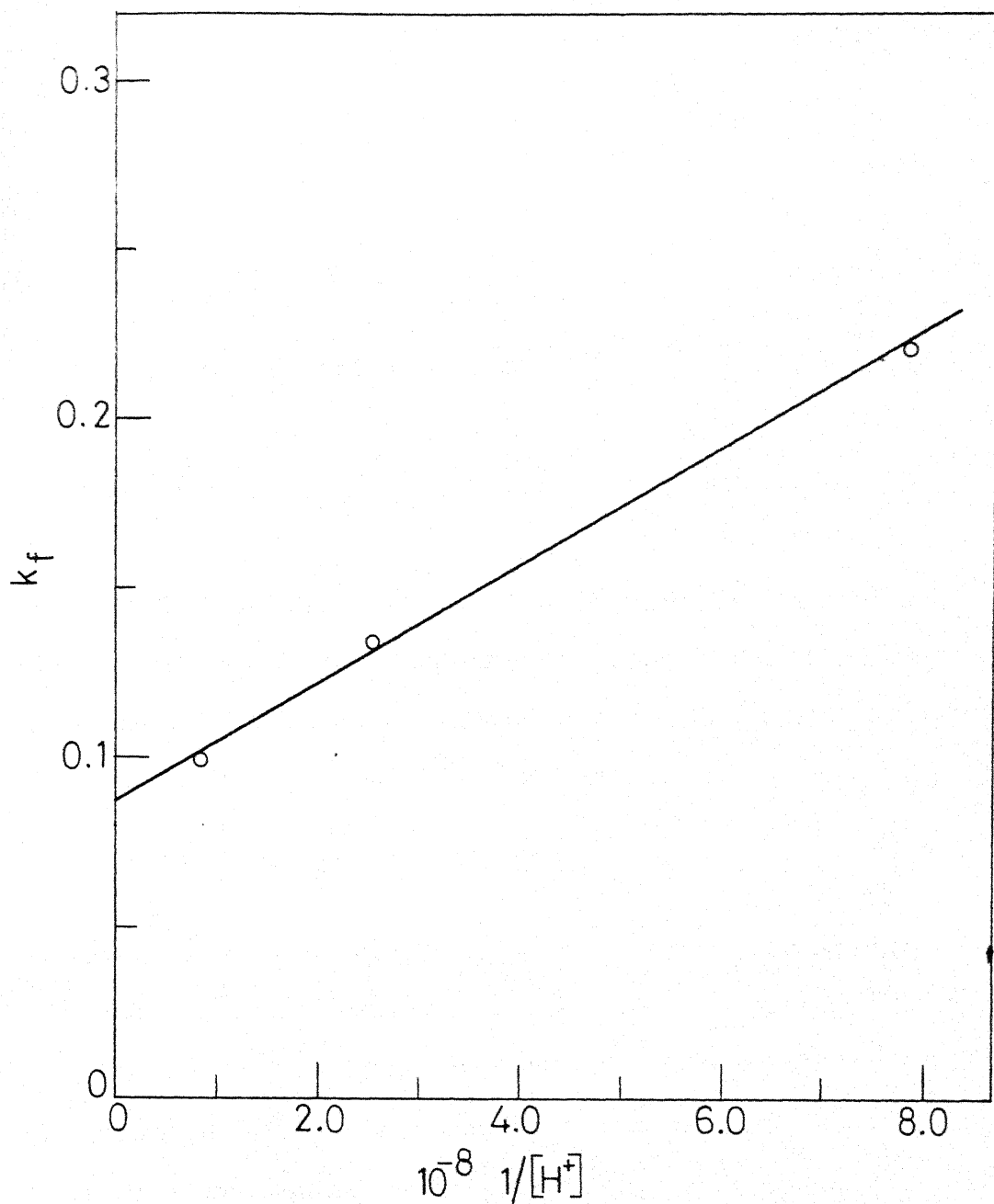
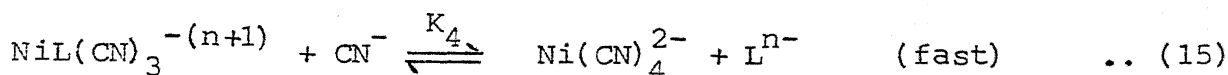
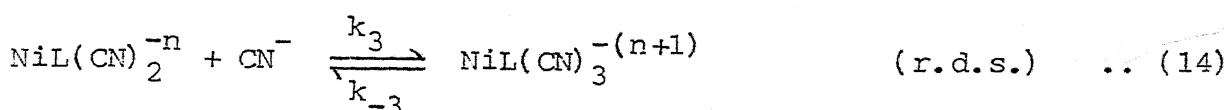
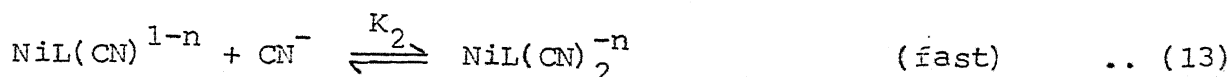
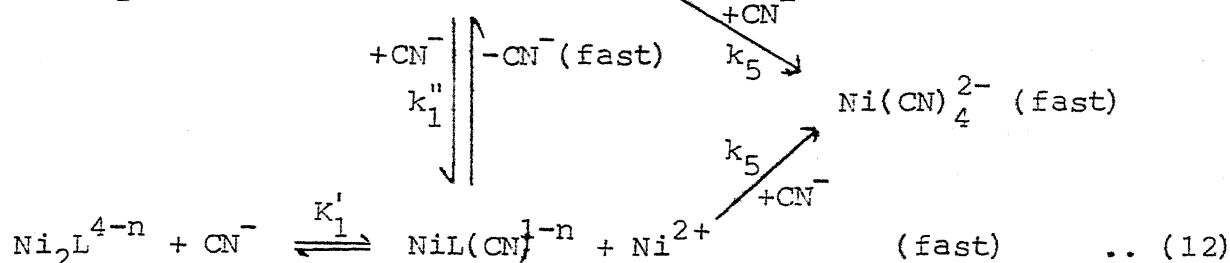
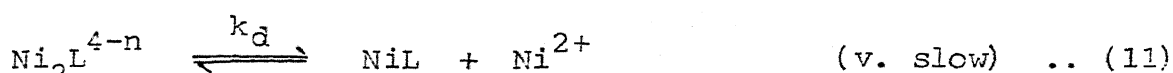
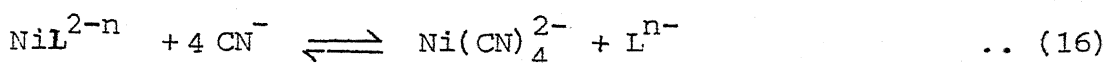


Fig. 111.7 Resolution of Rate Constants for the Reaction of Ni_2DTFA with Cyanide



Both the steps (11) ,& (12) and (13) are consistent with the experimental rate expression given in Equation (3). In Chapter II the kinetic results for the following mononuclear complex reaction (Eqn. 16) were reported.



where L were DTPA and TTHA. The reverse reaction for Ni_2L reactions also are the same as in the case of mononuclear complex reactions. There is no evidence for the formation of $\text{NiL}(\text{CN})_2$. The reverse rates are first order in $\text{Ni}(\text{CN})_4^{2-}$ and L^{n-} each and inverse first order in free cyanide. A consideration of both forward and reverse reaction rates leads us to a mechanistic Scheme given above (Eqns. 11-15).

A steady state treatment on the intermediate species $\text{NiL}(\text{CN})_3$, $\text{NiL}(\text{CN})$ and NiL gives a rate expression consistent

with the observed experimental rate law. The derivation is given in the following paragraph:

$$d[\text{Ni}(\text{CN})_4^{2-}]/dt = k_4[\text{NiL}(\text{CN})_3][\text{CN}^-] + k_d[\text{Ni}_2\text{L}] \quad \dots (17)$$

The second term corresponds to $\text{Ni}(\text{CN})_4^{2-}$ formation from dissociation of Ni_2L according to Eqn. (11).

$$\begin{aligned} d[\text{NiL}(\text{CN})_3]/dt &= k_3[\text{NiL}(\text{CN})_2][\text{CN}^-] - k_{-3}[\text{NiL}(\text{CN})_3] - \\ &\quad k_4[\text{NiL}(\text{CN})_3][\text{CN}^-] \\ &= K_2k_3[\text{NiL}(\text{CN})][\text{CN}^-]^2 - k_{-3}[\text{NiL}(\text{CN})_3] - \\ &\quad k_4[\text{NiL}(\text{CN})_3][\text{CN}^-] = 0 \quad \dots (18) \end{aligned}$$

$$\begin{aligned} d[\text{NiL}(\text{CN})]/dt &= k_1'[\text{Ni}_2\text{L}][\text{CN}^-] + k_1''[\text{NiL}][\text{CN}^-] - k_{-1}'[\text{NiL}(\text{CN})][\text{Ni}^{2+}] \\ &\quad - k_2[\text{NiL}(\text{CN})][\text{CN}^-] = 0 \quad \dots (19) \end{aligned}$$

The third term in this expression which contains product of two two very small concentration terms can be neglected in comparison to other terms. Therefore,

$$[\text{NiL}(\text{CN})] = \frac{k_1'[\text{Ni}_2\text{L}][\text{CN}^-] + k_1''[\text{NiL}][\text{CN}^-]}{k_2[\text{CN}^-]} \quad \dots (20)$$

From Equation (18)

$$[\text{NiL}(\text{CN})_3] = \frac{K_2k_3[\text{NiL}(\text{CN})][\text{CN}^-]^2}{k_{-3} + k_4[\text{CN}^-]} \quad \dots (21)$$

Substituting for $[\text{NiL}(\text{CN})]$ from Eqn. (20) in Eqn. (21)

$$[\text{NiL}(\text{CN})_3] = \frac{K_2k_3k_1'[\text{CN}^-]^3[\text{Ni}_2\text{L}] + K_2k_3k_1''[\text{NiL}][\text{CN}^-]^3}{k_2k_{-3}[\text{CN}^-] + k_2k_4[\text{CN}^-]^2} \quad \dots (22)$$

Also,

$$\frac{d[\text{NiL}]}{dt} = k_d[\text{Ni}_2\text{L}] - k_1''[\text{NiL}][\text{CN}^-] - k_d[\text{NiL}][\text{Ni}^{2+}] = 0$$

The third term is neglected again for reasons given above.

So,

$$[\text{NiL}] = \frac{k_d}{k_1''} \cdot \frac{[\text{Ni}_2\text{L}]}{[\text{CN}^-]} \quad \dots (24)$$

Substituting for NiL from Eqn. (24) in Eqn. (22)

$$[\text{NiL}(\text{CN})_3] = \frac{K_2 k_3 k_1' [\text{CN}^-]^3 [\text{Ni}_2\text{L}] + K_2 k_3 k_d [\text{Ni}_2\text{L}] [\text{CN}^-]^2}{K_2 k_{-3} [\text{CN}^-] + k_4 [\text{CN}^-]^2} \quad \dots (25)$$

Again substituting for $\text{NiL}(\text{CN})_3$ in rate Eqn. (17)

$$\begin{aligned} d[\text{Ni}(\text{CN})_4^{2-}]/dt &= k_4 \frac{K_2 k_3 k_1' [\text{Ni}_2\text{L}] [\text{CN}^-]^3 + K_2 k_3 k_d [\text{Ni}_2\text{L}] [\text{CN}^-]^2}{K_2 k_{-3} [\text{CN}^-] + k_4 [\text{CN}^-]^2} \times [\text{CN}^-] \\ &\quad + k_d [\text{Ni}_2\text{L}] \quad \dots (26) \end{aligned}$$

The second term in the numerator in the bracket and first term in the denominator of bracket can be neglected for reasons given in Chapter II. Finally,

$$\begin{aligned} \frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} &= \frac{K_2 k_3 k_1' [\text{Ni}_2\text{L}] [\text{CN}^-]^4}{[\text{CN}^-]^2} + k_d [\text{Ni}_2\text{L}] \\ &= K_2 k_3 k_1' [\text{Ni}_2\text{L}] [\text{CN}^-]^2 + k_d [\text{Ni}_2\text{L}] \\ &= k_2' [\text{Ni}_2\text{L}] [\text{CN}^-]^2 + k_d [\text{Ni}_2\text{L}] \\ &= \{k_2' [\text{CN}^-]^2 + k_d\} [\text{Ni}_2\text{L}] \end{aligned}$$

$$\text{where } k_2' = K_2 k_3 k_1'$$

This derived rate expression is in conformity with the experimental rate law given in Eqn. (3). Similarly a rate expression for $\text{Ni}_2(\text{DTPA})$ reaction can also be derived and is essentially similar.

A completely associative mechanism was considered by Stara and Kopanica^{18a} for Ni_2TTHA reaction, while in another

communication^{18b} on study of an electrophilic metal substitution reaction ($\text{Ni}_2\text{L} + 2 \text{Cu}^{2+} \rightleftharpoons \text{Cu}_2\text{L} + 2 \text{Ni}^{2+}$) they proposed the dissociation of Ni_2L to NiL and Ni^{2+} (aq.) followed by attack of Cu^{2+} .

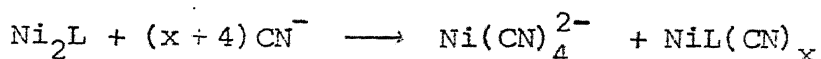
At the risk of repetition our objections to the mechanism given by Stara and Kopanica¹⁸ based on the following facts, are:

(1) Addition of dimethyl gloxime to a solution of Ni_2L in presence of small concentration of cyanide gives the characteristic precipitate of $\text{Ni}(\text{DMG})_2$ chelate. No such change is observed in absence of CN^- even on long standing. This shows the presence of Ni^{2+} (aq.) as a consequence of dissociation according to Equation (12).

(2) Addition of CN^- to about ten-fold excess of Ni_2TTHA gives the same product as obtained by similar addition of CN^- to NiTTHA . This product is $\text{NiTTHA}(\text{CN})^{5-}$ and its stoichiometry and stability constants have been established by the mole ratio method.²⁰ But in case of DTPA it could not be done as the characteristic peak of $\text{NiDTPA}(\text{CN})_2$ produced as an intermediate cannot be located. At the high cyanide concentration where this intermediate is produced, $\text{Ni}(\text{CN})_4^{2-}$ rapidly forms from $\text{NiL}(\text{CN})_2$. Therefore, no spectral evidence could be provided for its presence. But the order dependence of one in cyanide concentration for the forward reaction gives an unmistakable kinetic evidence for the same.

(3) A large absorbance change is observed immediately after mixing the reactants (i.e., Ni_2L and CN^-) as a result of

formation of $\text{Ni}(\text{CN})_4^{2-}$ not due to displacement of ligand from Ni_2L but due to cyanide assisted dissociation of Ni_2L according to Equation (12). This absorbance jump is equal to a value expected from Beer's law and stoichiometric conversion according to Equation:



(4) Kinetic investigations on the reactions of two bis-complexes viz. $\text{Ni}(\text{IDA})_2$ and $\text{Ni}(\text{MIDA})_2$ (where IDA is imino-diacetic acid and MIDA is N-methyl-iminodiacetic acid) with cyanide²² showed that the biscomplexes must first dissociate to give mixed complexes of the type $\text{NiL}(\text{CN})$ which react further with excess cyanide to produce $\text{Ni}(\text{CN})_4^{2-}$. Further, in the electrophilic substitution reaction (Eqn. 2) investigated by Stara and Kopanica,^{18b} they have themselves postulated dissociation of Ni_2TTHA to NiTTHA and $\text{Ni}^{2+}(\text{aquo})$ followed by other reaction steps.

The rather small activation energies of forward reactions (Table III.2) where cyanide dependence is second or first order shows an associative mechanism to be operative in which bond breaking and bond making is taking place simultaneously. This value is comparable to that of other mono(aminocarboxylato) $\text{Ni}(\text{II})$ reactions with CN^- investigated earlier.^{19, 20, 24, 25} As against this, the activation energies for dissociation according to Equation (11) are quite high (Table III.2).

From the foregoing discussion it is borne out that the substitution reaction of binuclear Ni(II) complex of TTHA & DTPA follows a different path than envisaged by Stara and Kopanica.^{18a} Our work has thrown interesting light on the behaviour of binuclear chelates in substitution processes. The net reaction in the present systems involves the cyanide assisted dissociation of binuclear complex followed by its conversion from an octahedral (or tetragonal) to a square planar complex. Three cyanides are required around central nickel ion to bring about the rate determining step while the fourth cyanide adds very rapidly to this displacing the remaining attached glycinate segment of aminocarboxylate and finally producing $\text{Ni}(\text{CN})_4^{2-}$.

A brief mention of pH dependence of these reactions would be in order. The reactions were run in a wide range of pH(7.0 - 11.5) to see the effect of pH on the reaction rates under conditions where order dependence with respect to cyanide is two or one in case of TTHA and DTPA reactions respectively. It was found that the rate decreases as pH decreases below pH 9.0 (Fig. III.5). This is due to the formation of a less reactive nucleophile viz., HCN. In the pH range 7 - 9 cyanide as well as HCN are reactants. Above pH 9 the rate levels off, which is due to reaction of cyanide ion as the principal reactive species as in case of our earlier studies (Chapter II). The rate constants due to reactions of CN^- and HCN have been resolved. In the rate determining step under conditions of high pH only one nitrogen of the ligand is attached to Ni^{2+} in addition to three cyanides.

However, at pH values less than 9 an intramolecular proton transfer seems to take place from HCN. This can be to any of unattached basic nitrogens of free glycinate segment and this will facilitate the unwrapping of TTHA or DTPA from the central nickel ion. Similar proton transfer was postulated in earlier studies¹⁻³ on mononuclear complexes also.

A summary of rate and equilibrium constants for the two reactions investigated are given in Table III.4.

Table III.4. Summary of the rate constants and equilibrium constants

	Ni ₂ TTHA	Ni ₂ DTPA
$K_{Ni_2L}^{NiL}$	$1.00 \times 10^{13*}$	$3.39 \times 10^5*$
k_d	$(1.63 \pm 0.03) \times 10^{-5}$	$(1.40 \pm 0.05) \times 10^{-4}$
$k_3 \text{ M}^{-1} \text{ s}^{-1}$		$(1.63 \pm 0.05) \times 10^{-1}$
$K_2 k_3 \text{ M}^{-2} \text{ s}^{-1}$	(10.15 ± 1.40)	
k_{CN}	$(10.15)^a$	1.77×10^{-1b}
k_{HCN}	2.4^a	8.60×10^{-2b}
$K_4^{-1} k_{-3} \text{ s}^{-1}$	$(3.08 \pm 0.17) \times 10^{-7c}$	$(4.78 \pm 0.6) \times 10^{-8c}$

*From Table II.2.

a) $\text{M}^{-2} \text{ s}^{-1}$; b) $\text{M}^{-1} \text{ s}^{-1}$; c) From Table II.13

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CHAPTER IV

KINETICS AND MECHANISM OF INTERCONVERSION OF MONO(POLYAMINE)NICKEL(II) AND TETRACYANO- NICKELATE(II) COMPLEXES IN ACIDIC MEDIA

ABSTRACT

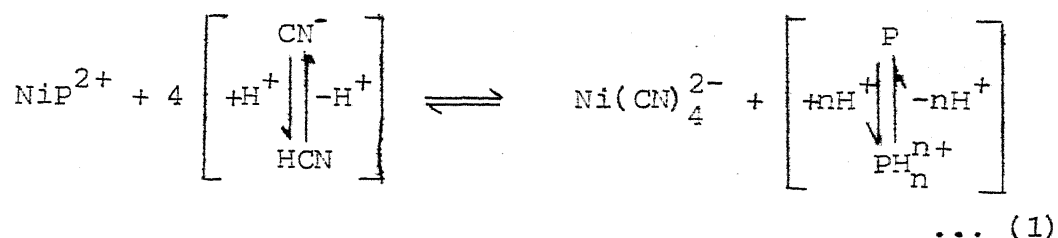
Second order kinetics are observed in the rate of formation of $\text{Ni}(\text{CN})_4^{2-}$ from polyamine $\text{Ni}(\text{II})$ complexes in the pH range 4.8-8.0 at $t = 25^\circ\text{C}$ and $\mu = 0.1 \text{ M}$ (NaClO_4). The polyamines used in this study are tetraethylenepentamine (Tet) and diethylenetriamine (Dien). The reaction is first order in $\text{Ni}(\text{polyamine})^{2+}$ and first order in total cyanide $\left\{ [\text{CN}^-]_{\text{T}} = [\text{CN}^-] + [\text{HCN}] \right\}$ over the pH range investigated. The reaction involves an initial rapid formation of mixed ligand intermediate $\text{NiP}(\text{CN})_x$ ($x = 1$ or 2) which then goes to the product. Like the nickel aminocarboxylate reactions, three cyanides are required around nickel ion for the rate determining step. Activation parameters have been obtained. The effect of pH has been investigated and the data have been interpreted accordingly.

IV.1 Introduction

The mechanisms of some nickel polyamine complex formation and dissociation reactions have been previously investigated.¹⁻⁵ The dissociation takes place in many steps essentially comprising alternation of nickel-nitrogen bond rupture followed by solvent occupation of the vacated site until all polyamine is displaced completely. The rate determining step has been identified to be the last nickel-nitrogen bond cleavage except in highly acidic conditions. Similarly, the rate determining step of the formation reaction is the solvent loss of metal ion immediately preceding the first nickel-nitrogen bond formation. The effect that coordinated nitrogens have upon rate of nickel-water substitution has also been studied.⁶⁻¹⁴ Polyamine nitrogens appear to accelerate water loss while aromatic ones do not.¹¹⁻¹⁴ Rorabacher¹⁵ has shown that experimentally measured rates of formation of some metal polyamines are faster than that predicted from Eigen mechanism¹⁶ due to internal conjugate base effect (ICB). The nature of this enhancement, and how other coordinated ligands effect it, is presently not well understood. Ligand exchange reactions involving nickel Tet-EDTA¹⁷ and TTHA,¹⁸ Nidien-EDTA,^{19,20} -TTHA,²¹ -DTPA, -CyDTA,²² -EDTA-OH,²⁰ -2,2'-bipy, -1,10-phen, -1,2',2''-terpy²³ and calm²⁴ have been studied. A considerable work is reported on the formation of $\text{Ni}(\text{CN})_4^{2-}$ from aminocarboxylates,²⁵⁻³⁴ polyamines,³⁵ phen,³⁶ triglycine³⁷ and some other ligands complexed to $\text{Ni}(\text{II})$ ^{38,39} and $\text{Ni}^{2+}(\text{aq.})$.^{40,41} Crouse and Margerum have studied the reaction of $\text{Ni}(\text{CN})_4^{2-}$

with various other ligands in presence and in absence of iodine as a scavenger⁴² for cyanide ion.

In the present study the kinetics of reaction (1) was investigated where P represents polyamines viz. Tet (tetraethylenepentamine) and Dien (diethylenetriamine):



IV.2 Experimental Section

Materials:

Diethylenetriamine (Eastman Kodak Co. U.S.A.) and tetraethylenepentamine (Sigma Chemicals, U.S.A.) were purified by distillation at reduced pressure.^{17,43} Doubly distilled deionized water was used for preparation of all solutions. The stock solutions of both polyamines were prepared and standardised potentiometrically as well as by the indicator method.

Nickel perchlorate and sodium cyanide solutions were prepared and standardised^{44,45} respectively as described in Chapter II. Sodium perchlorate was prepared and used for ionic strength control.

Nickel Polyamine Complexes

Solutions of nickel polyamine complexes were prepared by mixing stoichiometric amounts of nickel perchlorate and

polyamines.^{7,17,46} The pH of the solution was adjusted to the working pH by addition of HClO_4 . The concentrations of various species present in solution were calculated using a computer programme⁴⁷ and pK_a 's of polyamines and stability constants of their complexes with nickel(II) (Table IV.1) are shown in Figs. IV.1 and IV.2. It was verified that between pH 4.8-8.0, the mono complex of polyamine is the stable species. This observation was also supported by some previous studies.⁵²⁻⁵⁵

Kinetic Runs

All kinetic runs were carried out using Toshniwal spectrophotometer (Beckmann DU type) model RL-02, by following the increase in absorbance due to formation of $\text{Ni}(\text{CN})_4^{2-}$ at 267 and 285 nm. The reaction conditions were temp. = 25°C , pH=5.0 and $\mu = 0.1 \text{ M}$ (NaClO_4). A spectral study of reactants and products showed largest change in absorption at these wavelengths. It is reported in the literature that $\text{Ni}(\text{Tet})^{2+}$ ⁵⁶ and $\text{Ni}(\text{Dien})^{2+}$ ^{2,46} give peaks at 247, 545, 922 and 360, 595, 740, 959 nm respectively. We have observed these and some other peaks in the UV and visible spectra for mono and bis complexes (Figs. IV.3 and IV.4). Most of the kinetic data have been obtained at pH 5.0 and the pH dependence between pH 4.8 to 8.0 in case of NiTet and 4.8-6.5 in case of $\text{Ni}(\text{dien})$. Above these pH values reaction becomes too fast to be followed spectrophotometrically.

The forward reactions were run in presence of excess of cyanide and gave excellent psuedo first order plots

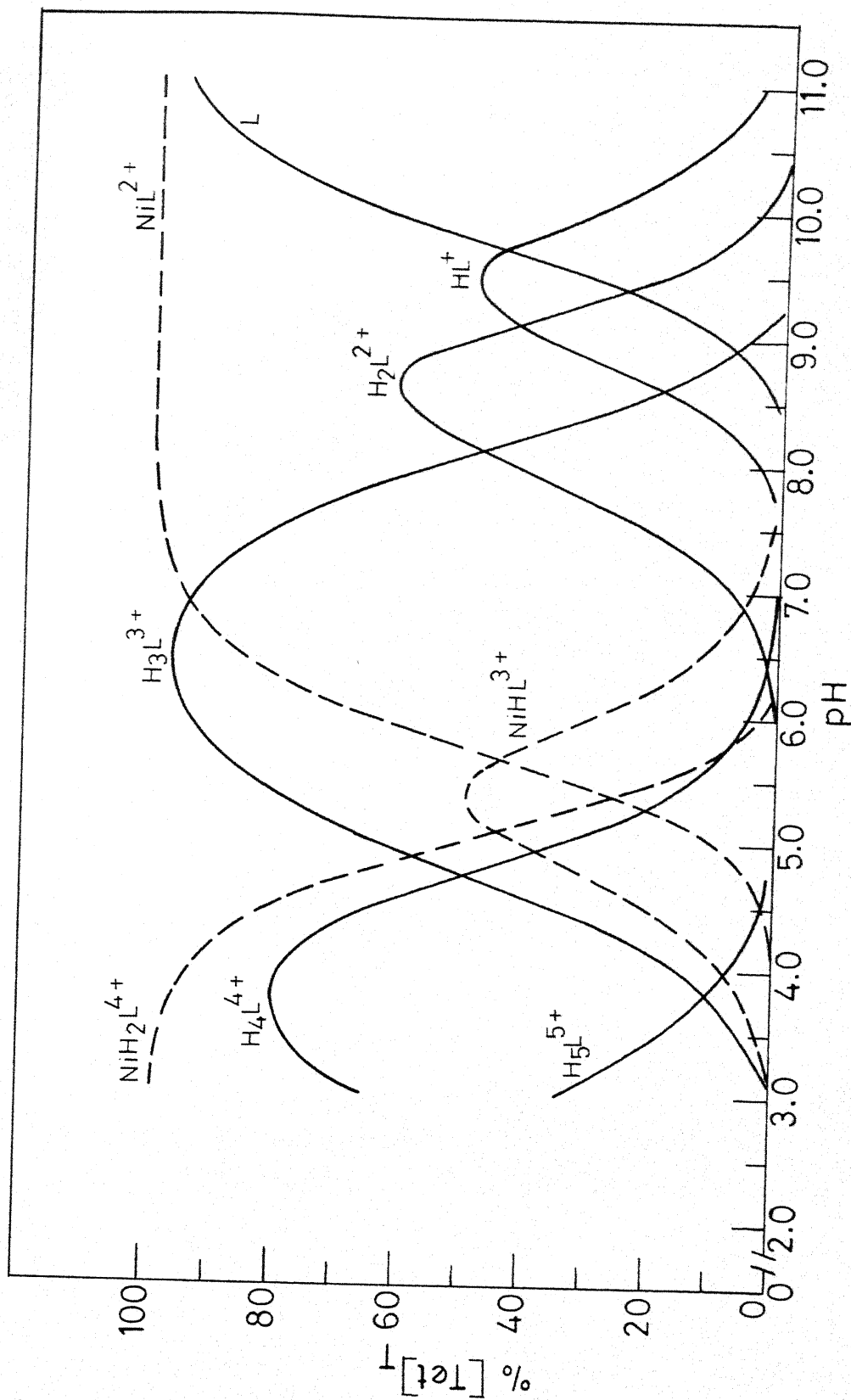


Fig. IV.1 Distribution of Protonated and Unprotonated Forms of Tet and NiTet^{2+} as a Function of pH; $[\text{Ni}^{2+}]_T = [\text{Tet}]_T = 5.0 \times 10^{-4} M$

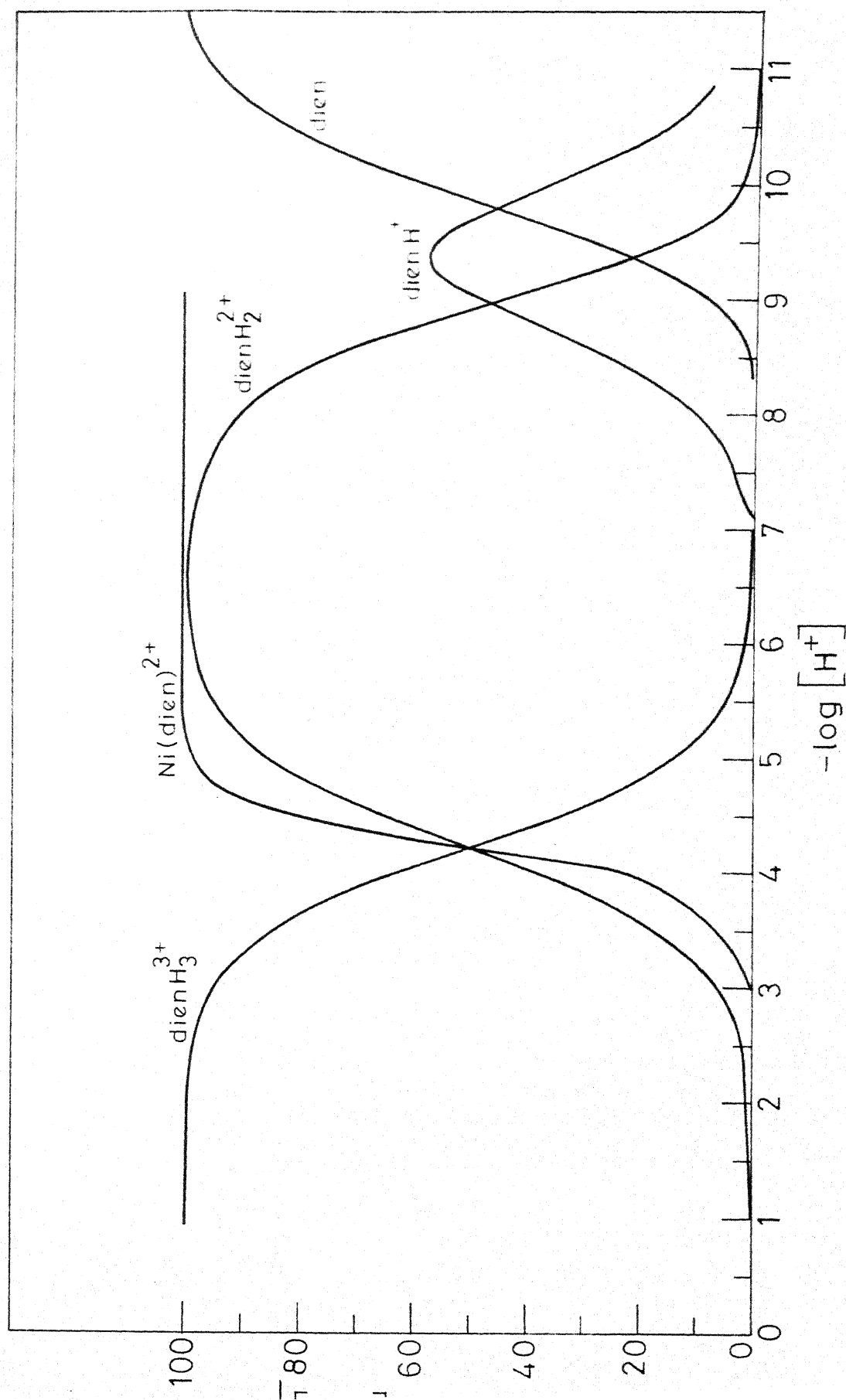


Fig. IV.2 Distribution of protonated and unprotonated forms of dien and Ni(dien)^{2+} complex as a function of pH, $[\text{Ni}^{2+}]_T = [\text{dien}]_T = 5.0 \times 10^{-4} \text{ M}$

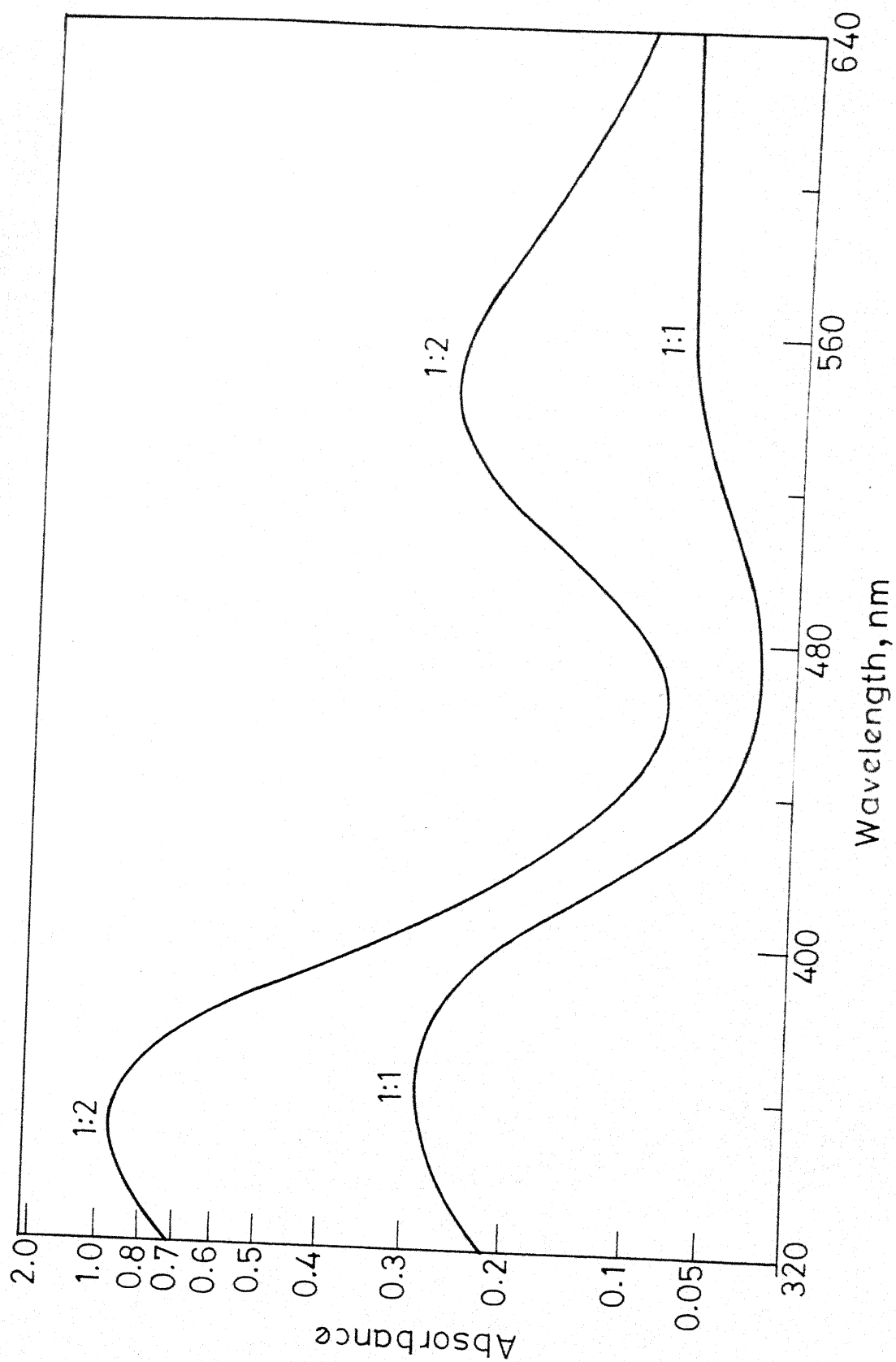


Fig. IV.3 Absorption Spectra of Ni(Tet)_2 and Ni(Tet)_2^{2+} Complexes

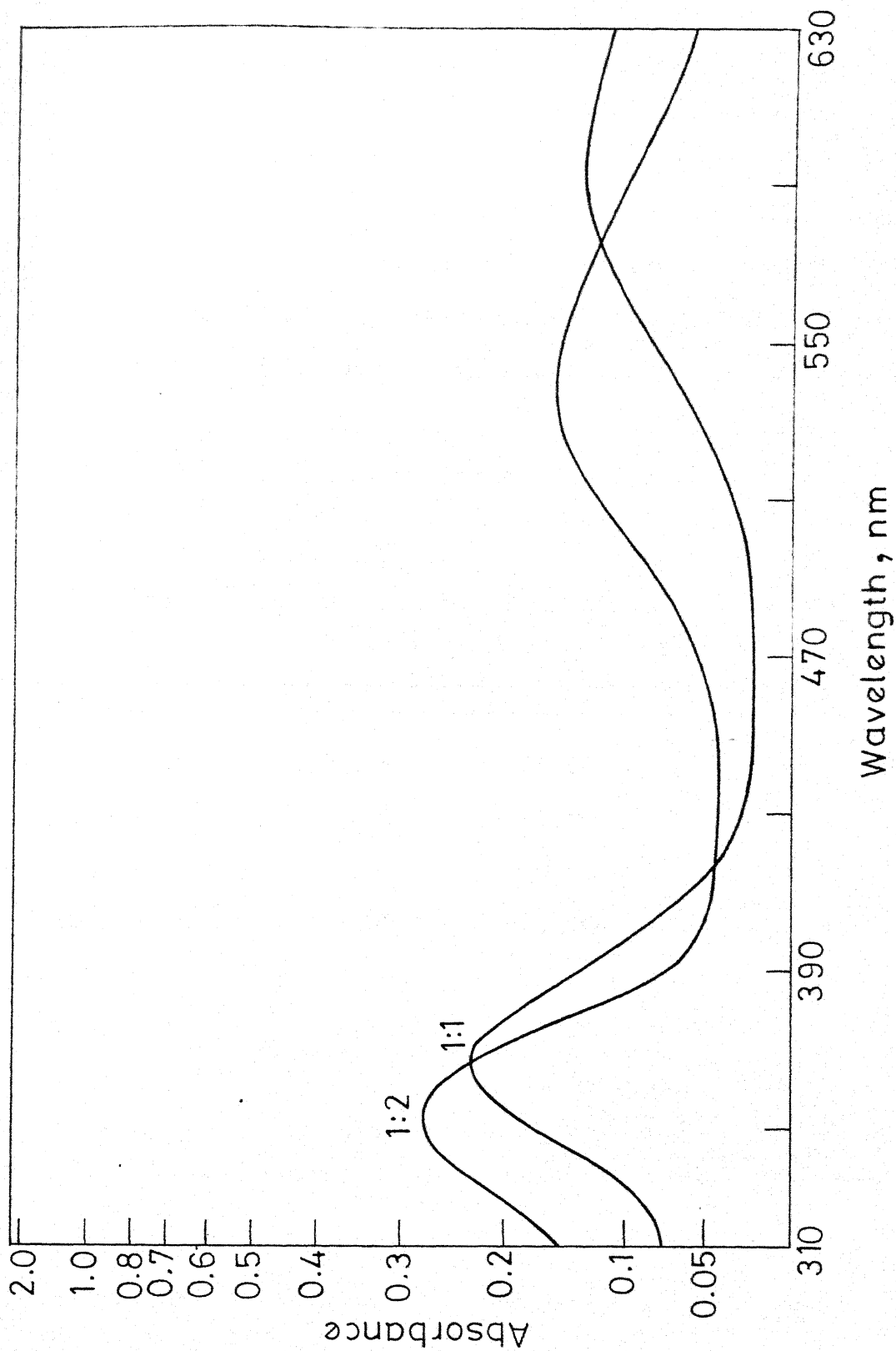


Fig. IV.4 Absorption Spectra of Ni(dien)_2^{2+} and Ni(dien)_2^{2+} Complexes

IV.3 ResultsReaction Orders in the Formation of $\text{Ni}(\text{CN})_4^{2-}$

The forward reaction in Equation (1) is first order in NiP^{2+} and first order in total uncomplexed cyanide where $[\text{CN}]_T = [\text{CN}^-] + [\text{HCN}]$ (Table IV.2 and Fig. IV.5). Table IV.2 shows that the observed first order rate constant, k_{obsd} , is independent of initial NiP^{2+} concentration, but is strongly dependent upon the total concentration of cyanide.

Table IV.2 Kinetics of formation of $\text{Ni}(\text{CN})_4^{2-}$ from mono(poly-amine)nickel(II) complexes using cyanide ion at temp = $25^\circ \pm 0.1^\circ\text{C}$; pH = 5.0 ± 0.1 ; $\mu = 0.1 \text{ M}$ (NaClO_4)
Polyamine: Tet (Tetraethylene pentamine)

$[\text{CN}^-]_T$	$10^5 [\text{NiP}]$	$k_{\text{obsd}}, \text{s}^{-1}$	$k_f, \text{M}^{-1}\text{s}^{-1}$
1	2	3	4
2.70×10^{-4}	6.45	5.21×10^{-4}	1.93
3.90×10^{-4}	6.45	7.90×10^{-4}	2.02
5.00×10^{-4}	7.50	9.97×10^{-4}	1.99
6.40×10^{-4}	7.50	1.00×10^{-3}	1.56
7.50×10^{-4}	6.45	1.07×10^{-3}	1.43
7.80×10^{-4}	6.45	1.30×10^{-3}	1.67
1.00×10^{-3}	6.45	1.85×10^{-3}	1.85
1.25×10^{-3}	6.45	1.97×10^{-3}	1.59
1.54×10^{-3}	7.50	2.15×10^{-3}	1.40
2.48×10^{-3}	6.12	2.23×10^{-3}	1.00
3.85×10^{-3}	6.45	3.85×10^{-3}	1.00

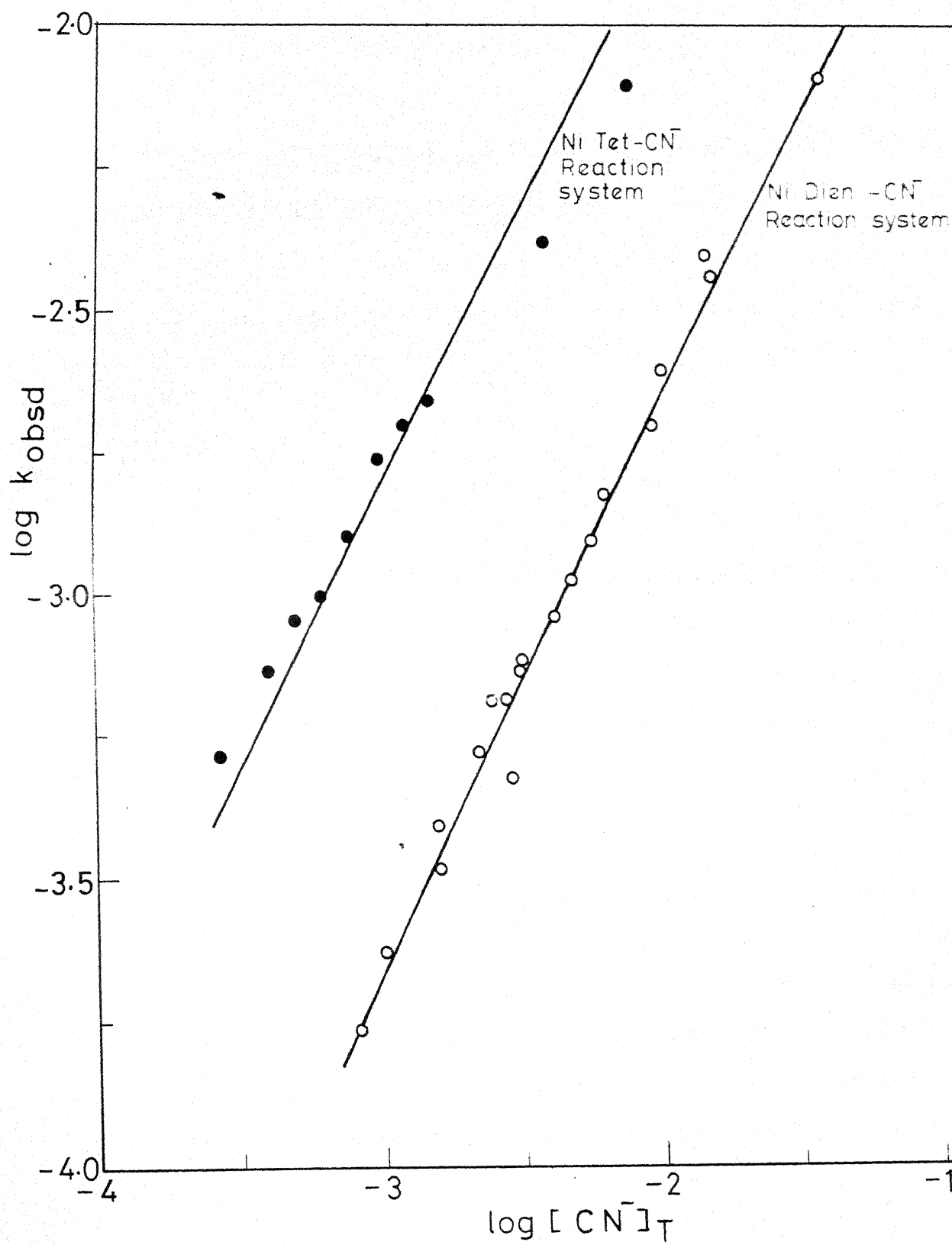
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Table IV.2 (contd.)

1	2	3	4
6.40×10^{-3}	8.62	7.66×10^{-3}	1.20
6.40×10^{-3}	7.50	7.60×10^{-3}	1.20
Av = (1.52 ± 0.09)			

Polyamine: Dien (Diethylenetriamine)

7.80×10^{-4}	7.25	1.70×10^{-4}	2.18×10^{-1}
1.00×10^{-3}	7.40	2.40×10^{-4}	2.40×10^{-1}
1.56×10^{-3}	3.70	4.60×10^{-4}	2.95×10^{-1}
1.60×10^{-3}	2.41	3.27×10^{-4}	2.04×10^{-1}
2.19×10^{-3}	4.82	5.49×10^{-4}	2.51×10^{-1}
2.19×10^{-3}	6.45	5.45×10^{-4}	2.49×10^{-1}
2.82×10^{-3}	6.65	6.72×10^{-4}	2.38×10^{-1}
3.13×10^{-3}	7.40	7.29×10^{-4}	2.33×10^{-1}
3.13×10^{-3}	4.83	7.51×10^{-4}	2.40×10^{-1}
4.53×10^{-3}	7.40	9.80×10^{-4}	2.16×10^{-1}
4.69×10^{-3}	6.45	1.06×10^{-3}	2.26×10^{-1}
5.65×10^{-3}	4.83	1.15×10^{-3}	2.04×10^{-1}
1.00×10^{-2}	6.45	2.53×10^{-3}	2.40×10^{-1}
1.47×10^{-2}	2.80	3.64×10^{-3}	2.48×10^{-1}
Av = (2.35 ± 0.05) $\times 10^{-1}$			



In all the kinetic runs, the initial absorbance after mixing was found to be higher than the calculated values based on the molar absorptivities of reagents. The higher initial absorbance can be attributed to the immediate formation of a mixed ligand complex of $\text{NiP}(\text{CN})_2$ type (here and in the following discussions no protons are indicated for simplicity) as in some other cases.²⁵⁻³⁵

The formation of mixed ligand $\text{NiP}(\text{CN})_2$ species appears to be complete during the course of mixing. A rate law (ignoring protons) reflecting this observation is given in Equation (2):

$$\begin{aligned} \frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} &= k_{\text{obsd}}[\text{NiP}(\text{CN})_2] \\ &= k_f[\text{NiP}(\text{CN})_2][\text{CN}^-]_T \end{aligned} \quad \dots (2)$$

The stability constants for these mixed complexes were determined as for aminocarboxylate reactions described in Chapter II.

At higher pH, the rates of formation of $\text{Ni}(\text{CN})_4^{2-}$ become so fast that it becomes difficult to use excess cyanide to determine the reaction order.

Kinetics of $\text{Ni}(\text{CN})_4^{2-}$ Dissociation in Presence of Polyamines

The disappearance of $\text{Ni}(\text{CN})_4^{2-}$ is greatly accelerated by the polyamine concentration in comparison to the much slower reaction of $\text{Ni}(\text{CN})_4^{2-}$ with aminocarboxylates²⁵⁻³¹ or perchloric acid.⁴⁰ The stability constants of nickel polyamine complexes (Table IV.1) are small in comparison to $\text{Ni}(\text{CN})_4^{2-}$.⁴⁰ A large

excess of polyamine is therefore, needed to force the reverse reaction. The reaction does not follow the simple rate law but it is first order each in $\text{Ni}(\text{CN})_4^{2-}$ and polyamine and inverse first order in cyanide according to the Eqn. (3) (Table IV.3 and Fig. IV.6):

$$-d[\text{Ni}(\text{CN})_4^{2-}]/dt = \frac{k_r [\text{Ni}(\text{CN})_4^{2-}] [\text{polyamine}]_T}{[\text{CN}^-]} \quad \dots (3)$$

Table IV.3. Rate of decomposition of $\text{Ni}(\text{CN})_4^{2-}$ in presence of polyamines at temp = 25°C ; pH = 5.0; $\mu = 0.1 \text{ M}$ (NaClO_4)

$10^3 [\text{Polyamine}]$	$10^8 k'_{\text{obsd}}, \text{M}^{-1} \text{sec}^{-1}$	$10^4 k_r, \text{s}^{-1}$
<u>(i) $\text{Ni}(\text{CN})_4^{2-}$ - Tetren System</u>		
$[\text{Ni}(\text{CN})_4^{2-}] = 7.80 \times 10^{-5} \text{ M}$		
0.36	4.31	1.19
0.72	9.00	1.25
1.44	22.00	1.53
2.88	35.70	1.24
		$A_v = (1.30 \pm 0.07)$
<u>(ii) $\text{Ni}(\text{CN})_4^{2-}$ - Dien System</u>		
$[\text{Ni}(\text{CN})_4^{2-}] = 7.76 \times 10^{-5} \text{ M}$		
1.00	3.80	0.38
1.25	6.00	0.41
6.00	25.20	0.42
7.50	34.00	0.45
12.50	57.40	0.46
		$A_v = (0.42 \pm 0.04)$

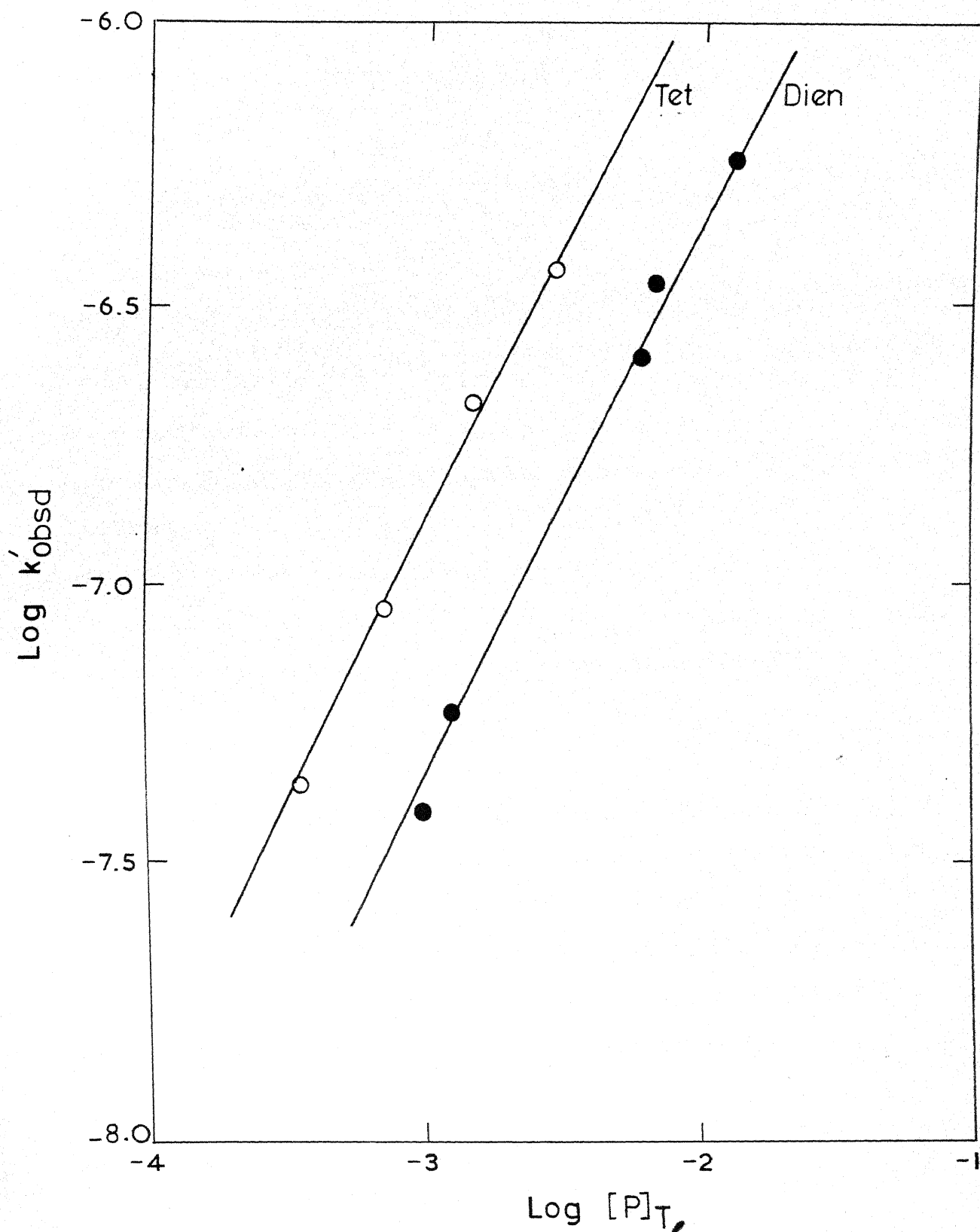


Fig. IV.6 Polyamine Dependence of Observed Reverse Rate Constants at $25 \pm 0.1^\circ\text{C}$; $\text{pH} = 5.0$ and $\mu = 0.1 \text{ M}$

Linear plots were obtained by using Eqn. (4):

$$(A_i - A_t) + A_i \ln \frac{A_t}{A_i} = -\frac{\epsilon l}{4} \cdot k'_{\text{obsd}} \cdot t \quad \dots (4)$$

which is integrated form of Equation (3). The notations are the same as used in Chapter II. Values of k'_{obsd} and k_r are given in Table IV.3.

Extrapolation of absorbance to zero time yielded an intercept lower than the value expected for $\text{Ni}(\text{CN})_4^{2-}$ initially present. This indicates again that an intermediate exists in equilibrium with $\text{Ni}(\text{CN})_4^{2-}$ prior to the rate determining step. This intermediate is assumed to be $\text{NiP}(\text{CN})_3$ (proton unassigned) in order to be consistent with the forward rate results. Similar observations were obtained in some previous studies^{25-31,33} as well.

Dependence of Forward and Reverse Rates on Temperature

Forward and reverse reactions were run in a range of temperature between 20°-45°C and it was found that they follow the Arrhenius equation (plots in Fig. IV.7 and IV.8). The activation parameters were calculated from these plots (Table IV.4) and used later in support of the proposed mechanism.

Effect of pH on the Forward Rates

Both the reactions were run in a wide range of pH and were seen to be strongly dependent on this variable. Values of pH higher than 8.0 in case of NiTet and 6.5 in case of NiDien

Table IV.4. Effect of temperature on forward and reverse Reactions. pH = 5.0; μ = 0.1 M (NaClO₄)

Temp. °C	$[\text{CN}^-]_T$	$k_{\text{obsd}}, \text{s}^{-1}$	Kinetic parameters
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(i) Forward Reaction

a. NiTet-Cyanide System

$$[\text{NiTet}] = 8.25 \times 10^{-5} \text{ M}; \text{ pH} = 5.0; \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

25 ± 0.1	3.20 × 10 ⁻⁴	8.80 × 10 ⁻⁴	E _a kcal; 5.84
	6.40 × 10 ⁻⁴	1.00 × 10 ⁻³	ΔH [‡] kcal; 5.25
30 ± 0.1	3.20 × 10 ⁻⁴	1.13 × 10 ⁻³	ΔS [‡] e.u.; -38.74
	6.40 × 10 ⁻⁴	1.65 × 10 ⁻³	pZ cm ⁻¹ ; 2.00 × 10 ⁴
35 ± 0.1	3.20 × 10 ⁻⁴	-	
	6.40 × 10 ⁻⁴	2.15 × 10 ⁻³	
40 ± 0.1	3.20 × 10 ⁻⁴	1.30 × 10 ⁻³	
	6.40 × 10 ⁻⁴	2.34 × 10 ⁻³	
45 ± 0.1	3.20 × 10 ⁻⁴	1.73 × 10 ⁻³	
	6.40 × 10 ⁻⁴	2.80 × 10 ⁻³	

b. Ni(Dien)²⁺-Cyanide System

$$[\text{Ni(Dien)}^{2+}] = 6.30 \times 10^{-5} \text{ M}; \text{ pH} = 5.0; \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

20 ± 0.1	3.13 × 10 ⁻³	3.58 × 10 ⁻⁴	E _a kcal; 12.03
	4.50 × 10 ⁻³	-	ΔH [‡] kcal; 11.44
25 ± 0.1	3.13 × 10 ⁻³	5.69 × 10 ⁻⁴	ΔS [‡] e.u.; -22.76
	4.50 × 10 ⁻³	9.40 × 10 ⁻⁴	pZ cm ⁻¹ ; 6.33 × 10 ⁷
30 ± 0.1	3.13 × 10 ⁻³	7.46 × 10 ⁻⁴	
	4.50 × 10 ⁻³	1.13 × 10 ⁻³	

...contd.

Table IV.4 (contd.)

35 \pm 0.1	3.13 $\times 10^{-3}$	1.10 $\times 10^{-3}$
	4.50 $\times 10^{-3}$	1.70 $\times 10^{-3}$
40 \pm 0.1	3.13 $\times 10^{-3}$	1.49 $\times 10^{-3}$
	4.50 $\times 10^{-3}$	3.00 $\times 10^{-3}$

(ii) Reverse Reaction

Temp. °C	[Polyamine]	$k'_{\text{obsd}}, \text{ s}^{-1}$	Kinetic Parameters
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a. $\text{Ni}(\text{CN})_4^{2-}$ -Tet System

$$[\text{Ni}(\text{CN})_4^{2-}] = 8.18 \times 10^{-5} \text{ M}; \text{ pH} = 5.0 \pm 0.1; \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

25 \pm 0.1	7.20 $\times 10^{-4}$	1.40 $\times 10^{-7}$	E_a kcal; 19.47
	2.88 $\times 10^{-3}$	3.57 $\times 10^{-7}$	ΔH^\ddagger kcal; 18.88
30 \pm 0.1	7.20 $\times 10^{-4}$	-	ΔS^\ddagger e.u.; -12.77
	2.88 $\times 10^{-3}$	5.63 $\times 10^{-7}$	pZ cm^{-1} ; 9.79×10^9
35 \pm 0.1	7.20 $\times 10^{-3}$	4.53 $\times 10^{-7}$	
	2.88 $\times 10^{-3}$	9.54 $\times 10^{-7}$	
40 \pm 0.1	7.20 $\times 10^{-4}$	7.12 $\times 10^{-7}$	
	2.88 $\times 10^{-3}$	1.91 $\times 10^{-6}$	
45 \pm 0.1	7.20 $\times 10^{-4}$	1.45 $\times 10^{-6}$	
	2.88 $\times 10^{-3}$	-	

b. $\text{Ni}(\text{CN})_4^{2-}$ -Dien System

$$[\text{Ni}(\text{CN})_4^{2-}] = 8.45 \times 10^{-5} \text{ M}; \text{ pH} = 5.0 \pm 0.1; \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

25 \pm 0.1	1.25 $\times 10^{-3}$	6.08 $\times 10^{-8}$	E_a kcal; 18.70
	6.32 $\times 10^{-3}$	3.00 $\times 10^{-7}$	ΔH^\ddagger kcal; 18.11
30 \pm 0.1	1.25 $\times 10^{-3}$	1.82 $\times 10^{-7}$	ΔS^\ddagger e.u.; -17.49
	6.32 $\times 10^{-3}$	4.40 $\times 10^{-7}$	pZ cm^{-1} ; 9.06×10^8

..contd.

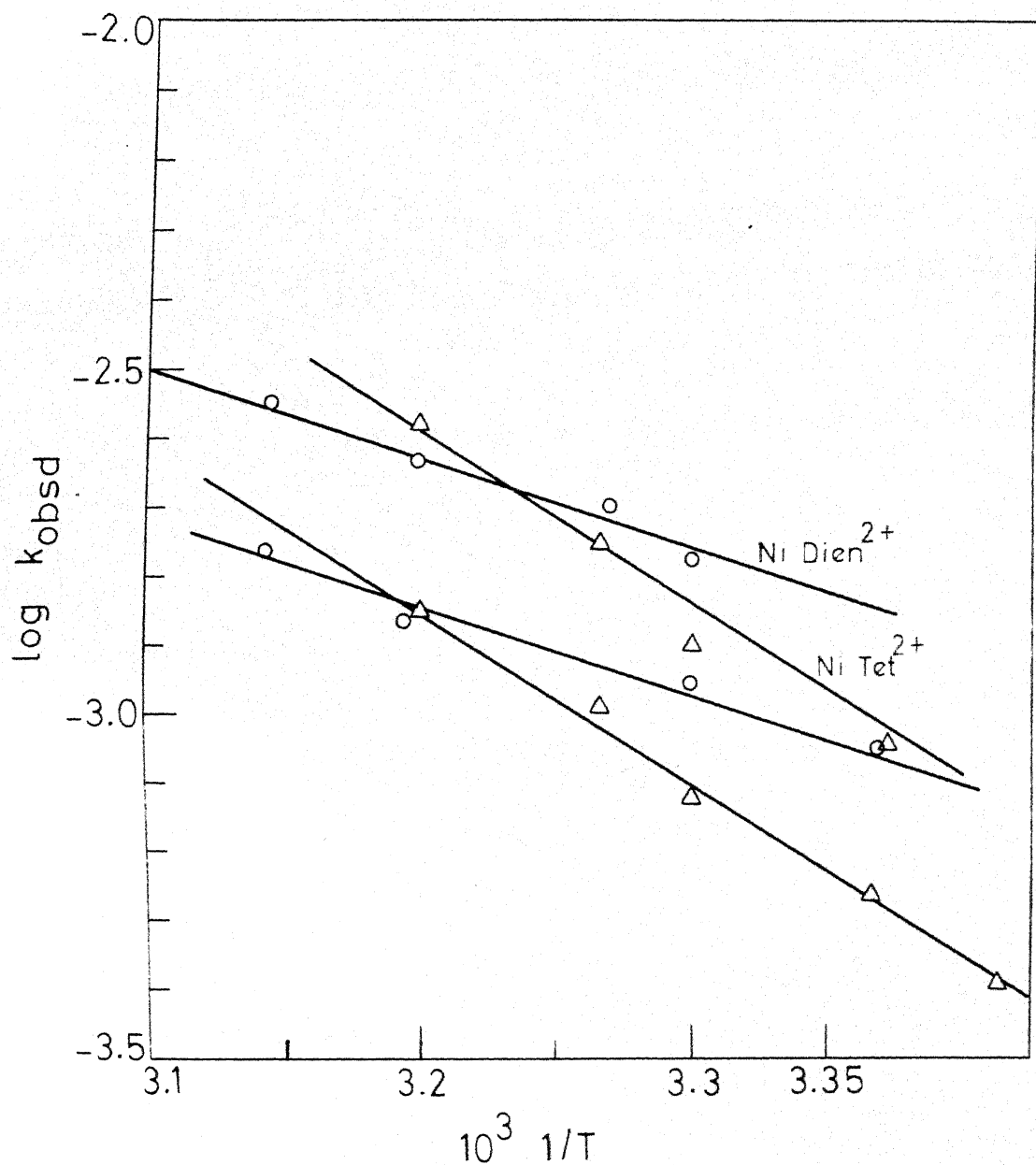


Fig. IV.7 Effect of Temperature on the Forward Reactions of $Ni^{2+}-CN^-$ Reaction Systems

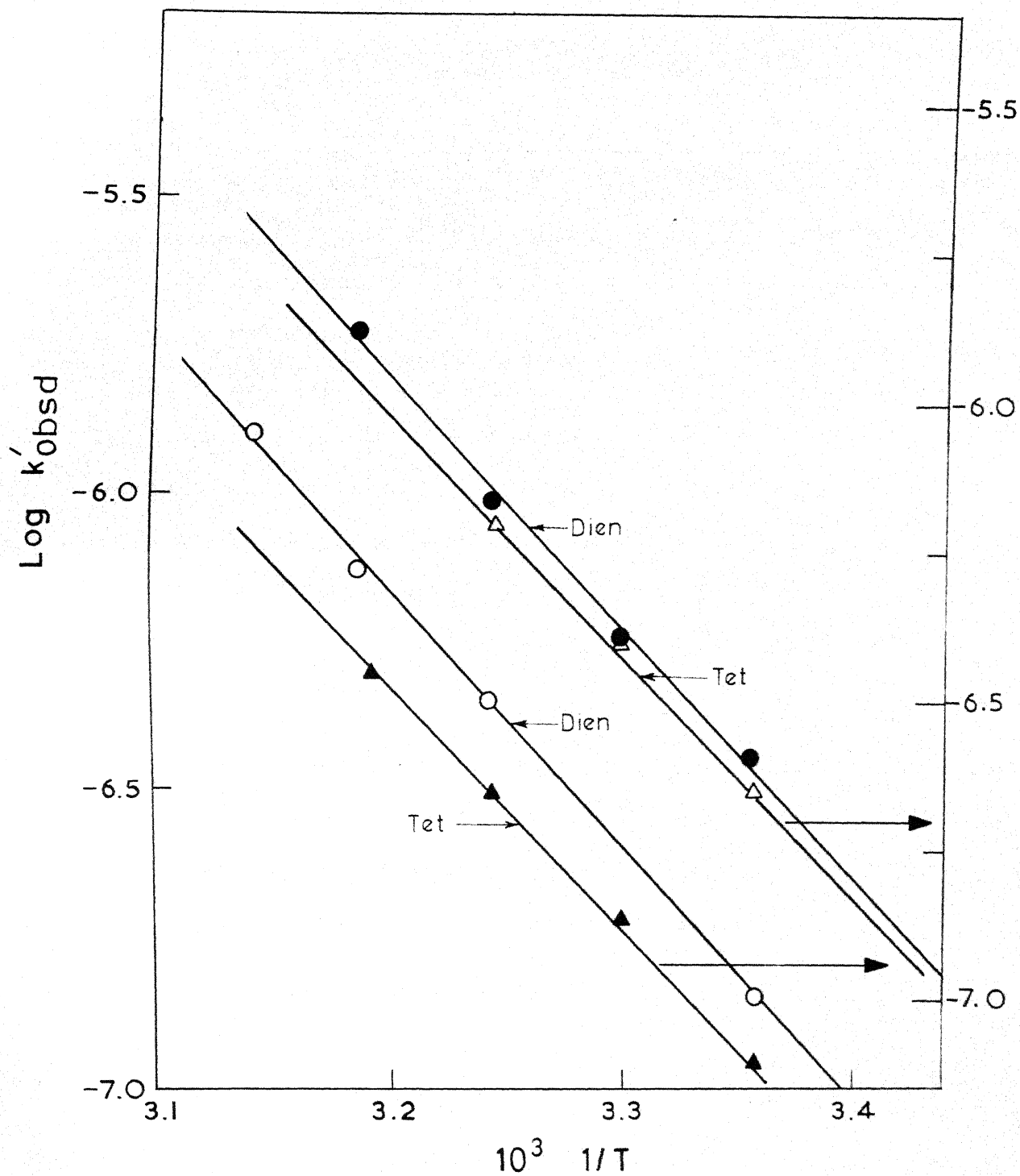


Fig. IV.8 Effect of Temperature on the Reaction of Polyamines with Ni(CO)_4

Table IV.4 (contd.)

35 \pm 0.1	1.25 $\times 10^{-3}$	2.10 $\times 10^{-7}$
	6.32 $\times 10^{-3}$	6.30 $\times 10^{-7}$
40 \pm 0.1	1.25 $\times 10^{-3}$	3.64 $\times 10^{-7}$
	6.32 $\times 10^{-3}$	-

were not practicable due to rapidity of these reactions above these pH values. It is found that the rate decreases as the pH decreases and this appears to be due to formation of the less reactive species HCN from cyanide ion. In case of NiTet reaction with cyanide it was found that the reaction rate does not fall linearly with decrease in pH (Table IV.5; Fig. IV.9). This may be analysed as follows:

$$\text{Rate} = \frac{d[\text{Ni}(\text{CN})_4^{2-}]}{dt} = k_f [\text{NiTet}]_T [\text{CN}]_T \quad \dots (5)$$

Here $[\text{NiTet}]_T$ and $[\text{CN}]_T$ include all protonated and unprotonated forms of NiTet and cyanide. It can be seen from Fig. IV.2 that the NiTet and NiHTet are the major species calculated purely on the basis of pK_a 's of these complexes (Table IV.1).

The rate of formation of $\text{Ni}(\text{CN})_4^{2-}$ can also be represented as

$$\begin{aligned} \text{Rate} &= d[\text{Ni}(\text{CN})_4^{2-}]/dt \\ &= k_{\text{CN}} \{ [\text{NiTet}] + [\text{NiHTet}] \} [\text{CN}^-] + k_{\text{HCN}} \{ [\text{NiTet}] + \\ &\quad + [\text{NiHTet}] \} [\text{HCN}] \quad \dots (6) \end{aligned}$$

$$= \left(k_{\text{CN}} \{ 1 + K_{\text{NiHTet}} [\text{H}^+] \} + k_{\text{HCN}} \{ 1 + K_{\text{NiHTet}} [\text{H}^+] \} \right. \\ \left. K_{\text{HCN}} [\text{H}^+] \right) [\text{NiTet}] [\text{CN}^-] \quad \dots (7)$$

$$= \{ k_{\text{CN}} + k_{\text{CN}} K_{\text{NiHTet}} [\text{H}^+] + k_{\text{HCN}} K_{\text{HCN}} [\text{H}^+] + \\ k_{\text{HCN}} K_{\text{HCN}} K_{\text{NiHTet}} [\text{H}^+]^2 \} [\text{NiTet}] [\text{CN}] \quad \dots (8)$$

Comparing Eqn. (5) and (8) we get

$$k_f [\text{NiTet}]_T [\text{CN}^-]_T = \{ k_{\text{CN}} \cdot k_{\text{CN}} \cdot K_{\text{NiHTet}} [\text{H}^+] + k_{\text{HCN}} K_{\text{HCN}} \\ [\text{H}^+] + k_{\text{HCN}} \cdot K_{\text{HCN}} K_{\text{NiHTet}} [\text{H}^+]^2 \} \\ [\text{NiTet}] [\text{CN}^-] \quad \dots (9)$$

Rearranging Eqn. (9)

$$k_f \cdot \frac{[\text{NiTet}]_T [\text{CN}^-]_T}{[\text{NiTet}] [\text{CN}^-]} = k_{\text{CN}} + (k_{\text{CN}} K_{\text{NiHTet}} + k_{\text{HCN}} K_{\text{HCN}}) [\text{H}^+] \\ + k_{\text{HCN}} \cdot K_{\text{HCN}} K_{\text{NiHTet}} [\text{H}^+]^2 \\ = k_1 + k_2 [\text{H}^+] + k_3 [\text{H}^+]^2 \quad \dots (10)$$

where k_1 , k_2 and k_3 are collections of appropriate constants viz., k_{CN} , k_{HCN} , K_{HCN} and K_{NiHTet} . Equation (10) is not a simple relationship but at lower pH the plot of k_f versus $[\text{H}^+]$ (or $\log k_f$ versus $-\log [\text{H}^+]$) should give a near parabolic curve which is actually found to be the case (Fig. IV.9). At higher pH the L.H.S. will be equal to k_f while the squared term in $[\text{H}^+]$ can be ignored. Then Eqn. (10) takes the form:

$$k_f = k_1 + k_2 [\text{H}^+] \quad \dots (10a)$$

Table IV.5. Effect of pH on forward and reverse rates
at temp. = $25 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ M (NaClO}_4\text{)}$

pH	k_{obsd}	$k_f = \frac{k_{\text{obsd}}}{[\text{CN}^-]_T}$
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(i) Forward Reaction:

(a) Ni(Tet)²⁺-Cyanide System

$$[\text{Ni(Tet)}^{2+}] = 5.20 \times 10^{-5} \text{ M}; [\text{CN}^-]_T = 6.50 \times 10^{-4} \text{ M.}$$

4.50	2.76×10^{-4}	0.42
5.00	9.88×10^{-4}	1.52
5.50	1.30×10^{-3}	2.00
6.00	1.90×10^{-3}	2.93
6.50	2.45×10^{-3}	3.77
7.00	3.45×10^{-3}	5.31
7.50	5.76×10^{-3}	8.86
8.00	1.51×10^{-2}	23.19

(b) Ni(Dien)-Cyanide System

$$[\text{Ni(Dien)}^{2+}] = 4.31 \times 10^{-5} \text{ M}; [\text{CN}^-]_T = 1.95 \times 10^{-3} \text{ M}$$

4.6	2.30×10^{-4}	1.18×10^{-1}
5.0	2.98×10^{-4}	1.53×10^{-1}
5.5	9.61×10^{-4}	4.93×10^{-1}
5.8	1.61×10^{-3}	8.26×10^{-1}
6.0	2.47×10^{-3}	12.70×10^{-1}

(ii) Reverse Reaction:

(a) Ni(CN)₄²⁻ - Tetren System temp. = $25 \pm 0.1^\circ\text{C}$; $\mu = 0.5 \text{ M (NaClO}_4\text{)}$

$$[\text{Ni(CN)}_4^{2-}] = 9.05 \times 10^{-5} \text{ M}; [\text{Tet}] = 2.88 \times 10^{-3} \text{ M}$$

4.7	2.16×10^{-7}	7.50×10^{-5}
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...contd.

Table IV.5 (contd.)

5.0	3.57×10^{-7}	1.24×10^{-4}
5.5	9.50×10^{-7}	3.30×10^{-4}
6.0	1.28×10^{-6}	4.44×10^{-4}
6.5	1.50×10^{-6}	5.21×10^{-4}

(b) $\text{Ni}(\text{CN})_4^{2-}$ -Dien System

$$[\text{Ni}(\text{CN})_4^{2-}] = 8.50 \times 10^{-5} \text{ M}; [\text{Dien}]_T = 6.32 \times 10^{-3} \text{ M}$$

4.7	1.40×10^{-7}	2.21×10^{-5}
5.0	2.20×10^{-7}	3.48×10^{-5}
5.5	4.40×10^{-7}	6.96×10^{-5}
6.0	1.21×10^{-6}	19.20×10^{-5}

In high pH region a plot of $\log k_{\text{obsd}}$ vs pH

At high pH region one ^{be} should get a straight line. Values of k_f around pH 8 give a line with a slope equal to one which indicates that one HCN is a reactant in this pH region. The values of rate constants were resolved in this region as in case of Dien (given below). The value of k_{CN} is $260 \text{ M}^{-1} \text{ s}^{-1}$ and k_{HCN} is $1.52 \text{ M}^{-1} \text{ s}^{-1}$.

Similarly, the pH effect was seen on the Dien reaction also. It was found from the plot of $\log k_{\text{obsd}}$ versus $-\log [\text{H}^+]$ that the slope is equal to one. It is inferred, therefore, that in the working pH range one HCN is a reactant until the rate determining step. The results can be interpreted as follows:

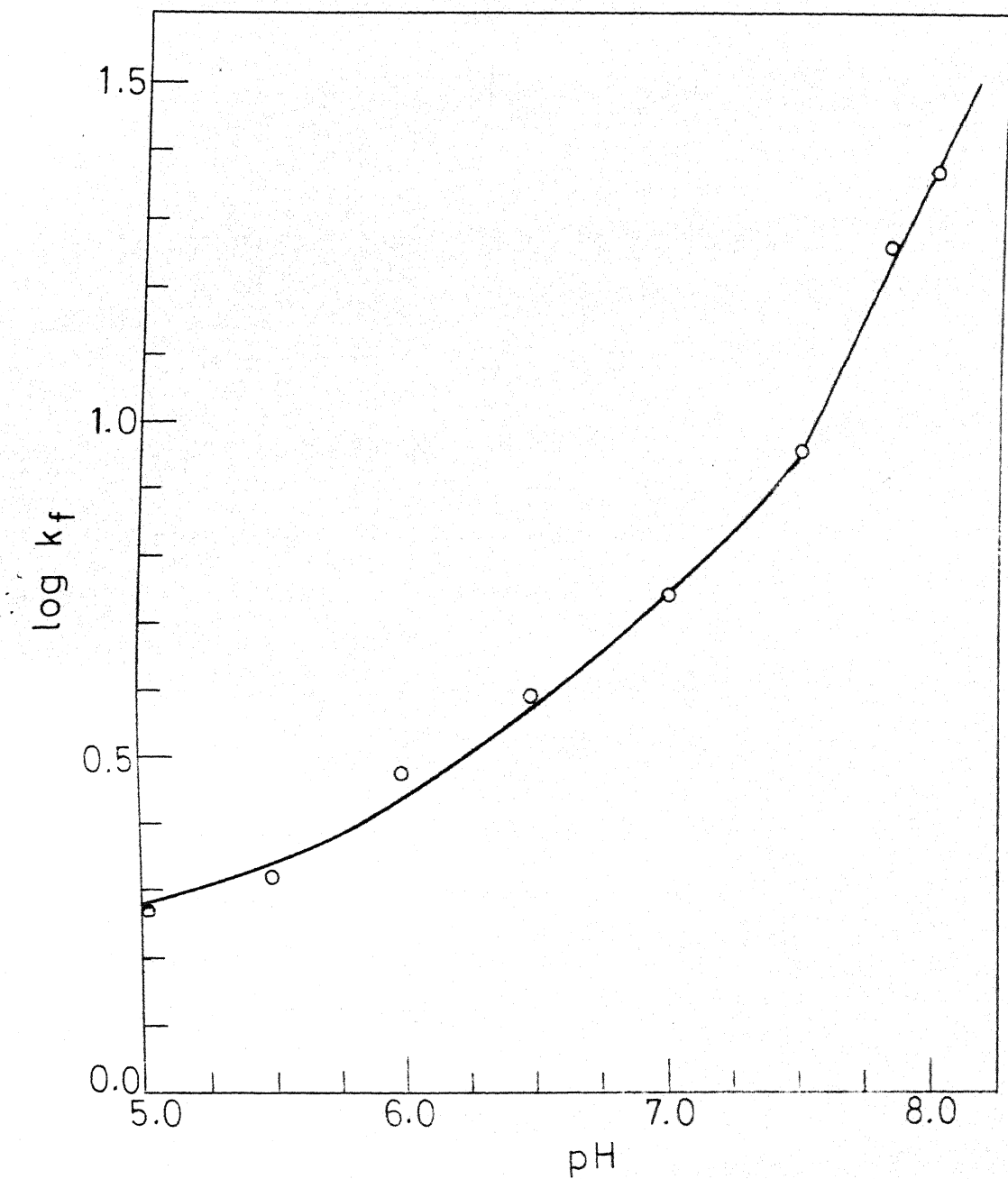


Fig. 11.9 Effect of pH on the Reaction of NiTet^{2+} with Cyanide

$$k_f [\text{CN}]_T = k_{\text{CN}} [\text{CN}] + k_{\text{HCN}} [\text{HCN}] \quad \dots (11)$$

$$k_f \{ [\text{CN}] + [\text{HCN}] \} = k_{\text{CN}} [\text{CN}] + k_{\text{HCN}} [\text{HCN}]$$

Dividing throughout by $[\text{HCN}]$

$$k_f \left\{ \frac{[\text{CN}]}{[\text{HCN}]} + 1 \right\} = k_{\text{CN}} \frac{[\text{CN}]}{[\text{HCN}]} + k_{\text{HCN}} \quad \dots (12)$$

$$k_f \left\{ 1 + \frac{1}{K_{\text{HCN}} [\text{H}^+]} \right\} = \frac{k_{\text{CN}}}{K_{\text{HCN}}} \cdot \frac{1}{[\text{H}^+]} + k_{\text{HCN}} \quad \dots (13)$$

where K_{HCN} is the protonation constant of cyanide ion.

The second term on the L.H.S. can be neglected in comparison to 1 except at high pH values. Therefore, Eqn. (13) takes the form

$$k_f = \frac{k_{\text{CN}}}{K_{\text{HCN}}} \cdot \frac{1}{[\text{H}^+]} + k_{\text{HCN}} \quad \dots (14)$$

The plot of Equation (14) is shown in Fig. IV.10. The slope of this line gives the values of $k_{\text{CN}}/K_{\text{HCN}}$ from which one can calculate the rate constant k_{CN} equal to $1.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The intercept of the line gives the value of k_{HCN} equal to $0.07 \text{ M}^{-1} \text{ s}^{-1}$. *The uncertainty of the latter value is rather large.*

Effect of pH on the Reverse Reaction

The reverse reaction was run in a range of pH 5 to 7 to see the effect of hydrogen ion concentration and it was found that the rate of reverse reaction is also dependent on pH. The plot of $\log k'_{\text{obsd}}$ versus $-\log [\text{H}^+]$ gives a straight line in case of both reactions having a slope equal to one and the reaction

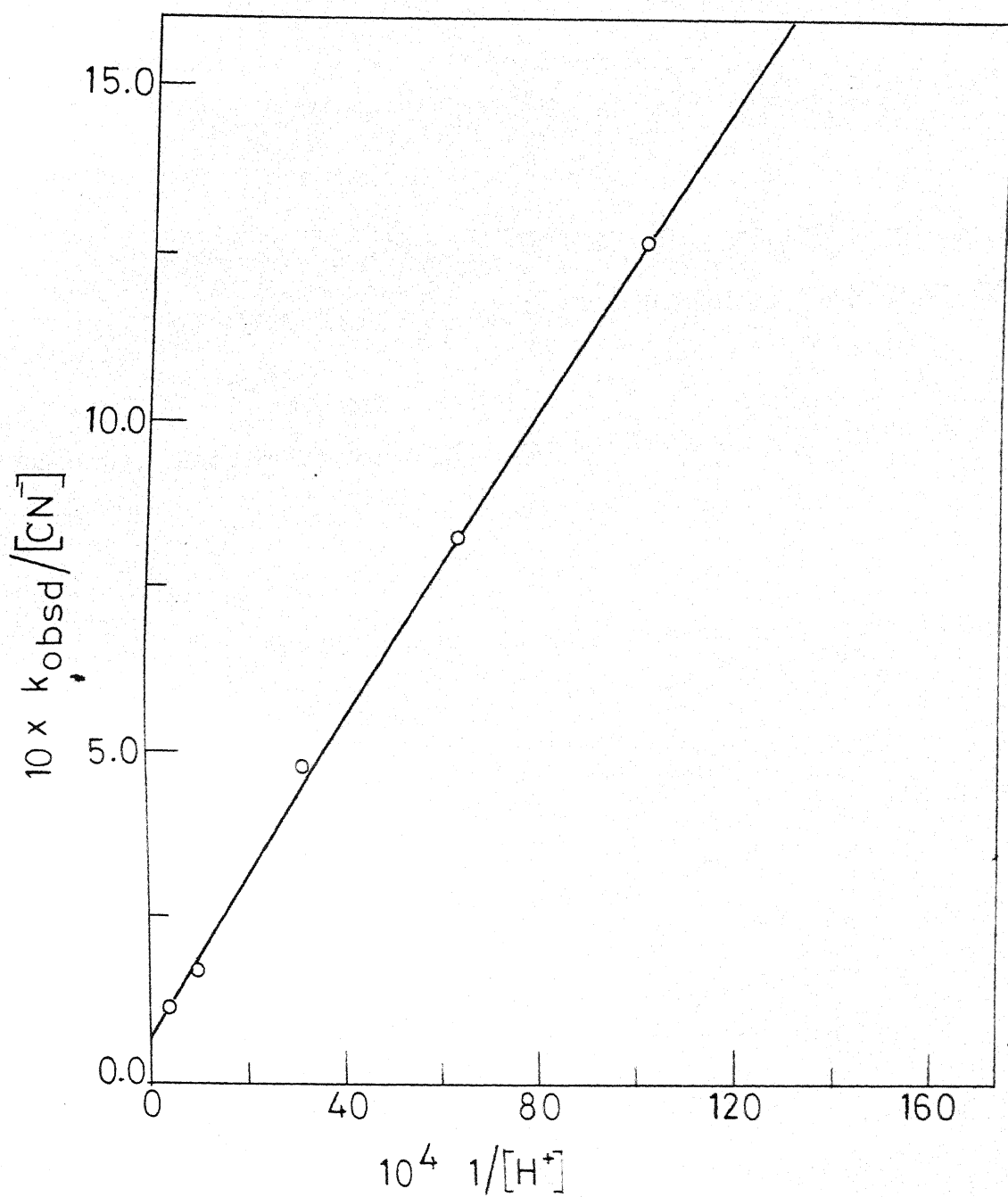


Fig. IV.10 Effect of pH on the Reaction of Co^{2+} with Cyanide

rate was found to decrease with decrease in pH. The neutral polyamine molecules would be expected to react more rapidly with $\text{Ni}(\text{CN})_4^{2-}$ complex than their protonated forms. If the reactant were polyamine only, k'_{obsd} would vary as $1/[\text{H}^+]^2$ or $1/[\text{H}^+]^3$ in case of Tetren reaction in the pH range 5 - 7. In case of Dien, however, it would vary as $1/[\text{H}^+]$ or $1/[\text{H}^+]^2$ around pH 5. Therefore, TetH_2^{2+} and TetH_3^{3+} are reactants in case of Tet reaction with $\text{Ni}(\text{CN})_4^{2-}$ while DienH^+ and DienH_2^{2+} are reactants in the latter reaction. The rate constants have been resolved as follows:

$$k_r [\text{Tet}]_T = k_{\text{H}_2\text{Tet}} [\text{H}_2\text{Tet}] + k_{\text{H}_3\text{Tet}} [\text{H}_3\text{Tet}] \quad \dots (15)$$

$$k_r \left\{ [\text{HTet}] + [\text{H}_2\text{Tet}] + [\text{H}_3\text{Tet}] \right\} = k_{\text{H}_2\text{Tet}} [\text{H}_2\text{Tet}] + k_{\text{H}_3\text{Tet}} [\text{H}_3\text{Tet}] \quad \dots (16)$$

$$\begin{aligned} \text{or, } k_r \left\{ \frac{1}{\frac{K_{\text{H}_2\text{Tet}}}{[\text{HTet}]} \cdot \frac{K_{\text{H}_3\text{Tet}}}{[\text{H}_2\text{Tet}]}} \cdot \frac{1}{[\text{H}^+]^2} + \frac{1}{\frac{K_{\text{H}_3\text{Tet}}}{[\text{H}_2\text{Tet}]} \cdot \frac{1}{[\text{H}^+]}} + 1 \right\} \\ = \frac{k_{\text{H}_2\text{Tet}}}{\frac{K_{\text{H}_3\text{Tet}}}{[\text{H}_2\text{Tet}]} \cdot \frac{1}{[\text{H}^+]}} + k_{\text{H}_3\text{Tet}} \quad \dots (17) \end{aligned}$$

where $\frac{K_{\text{H}_2\text{Tet}}}{K_{\text{HTet}}}$ and $\frac{K_{\text{H}_3\text{Tet}}}{K_{\text{H}_2\text{Tet}}}$ are protonation constants for respective

equilibria. The plot of L.H.S. of Equation (17) versus $1/[H^+]$ gives a straight line (Fig. IV.11) and the resolved rate constants k_{H_2Tet} and k_{H_3Tet} can be calculated from the slope and intercept of this line. The values of k_{H_2Tet} and k_{H_3Tet} determined in this manner are 0.10 & $1.01 \times 10^{-5} s^{-1}$ respectively. Similarly, for Dien reaction also an equation can be derived whose final form is given in Equation (18):

$$k_r \left\{ 1 + \frac{1}{K_{H_2Dien}^{H_{Dien}}} \cdot \frac{1}{[H^+]} \right\} = k_{HDien} \frac{1}{K_{H_2Dien}^{H_{Dien}}} \cdot \frac{1}{[H^+]} + k_{H_2dien} \quad \dots (18)$$

The second term in the L.H.S. bracket can be neglected in comparison to 1 and Equation (18) takes the form

$$k_r = k_{HDien} \frac{1}{K_{H_2Dien}^{H_{Dien}}} \cdot \frac{1}{[H^+]} + k_{H_2dien} \quad \dots (19)$$

The plot of k_r versus $1/[H^+]$ (Equation 19)) makes it possible to resolve the rate constants from Fig. IV.11. The values of k_{HDien} and k_{H_2dien} are found to be equal to 2.02 and $6.0 \times 10^{-6} s^{-1}$ respectively. The decrease in rate is due to formation of the protonated forms of polyamines which are less reactive than unprotonated forms.

IV.4 Discussion

Margerum et al.^{3,35} have reported that the acid dissociation of NiP^{2+} [where P is Tet, Trien and Dien] is negligible

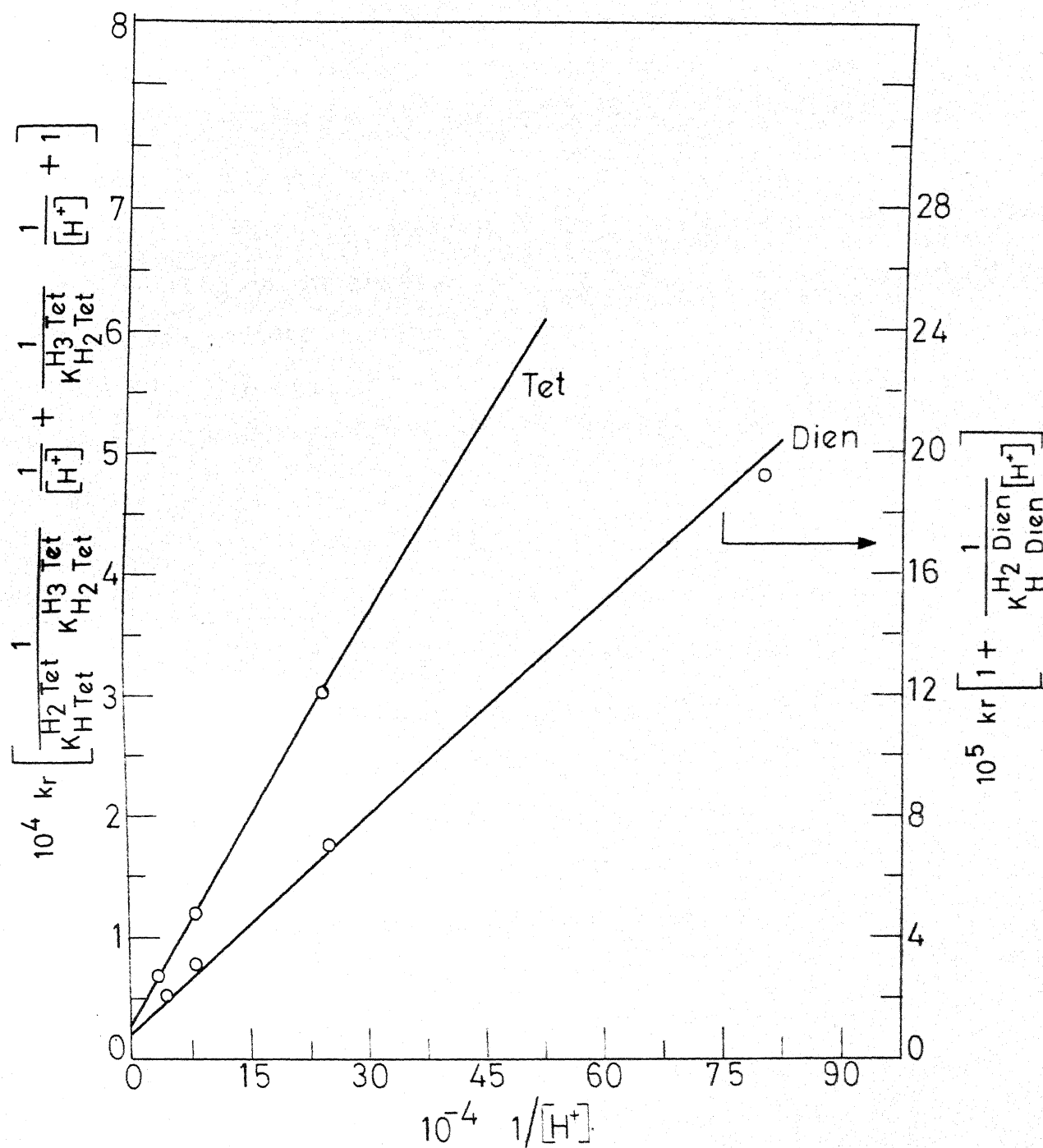


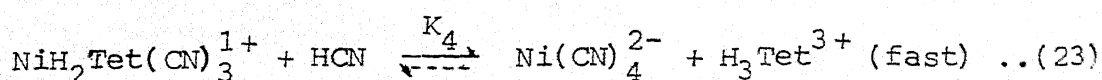
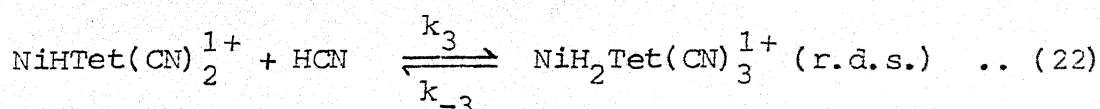
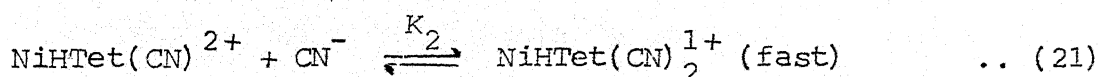
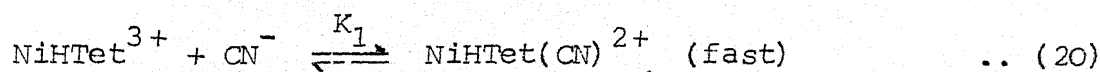
Fig. IV.11 Effect of pH on the Reaction of $Ni(CN)_4^{2-}$ with Polyamines

at low acid concentration (\sim pH 5). The observed dependence is first order in $[\text{CN}^-]_{\text{T}}$ which points to the presence of a mixed ligand complex $\text{NiP}(\text{CN})_2$ (proton unassigned) as a reactant which on further reaction with HCN produces the intermediate $\text{NiP}(\text{CN})_3$ and finally $\text{Ni}(\text{CN})_4^{2-}$ and free or protonated polyamines. The observations on the reverse reaction also show the presence of the above intermediate (similar to mono(amino)carboxylatonickel(II) reactions with cyanide ion; cf. Chapter II). The positioning of three cyanide around Ni^{2+} appears to be the rate controlling factor.

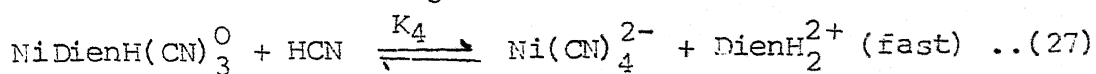
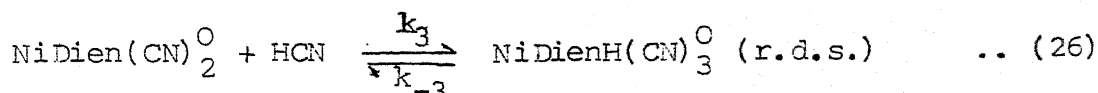
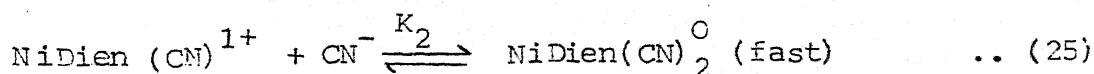
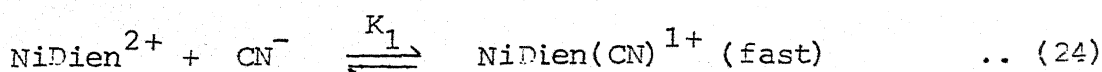
The pH dependence of the rate constants for forward rate shows that two cyanides are reactants in addition to one HCN upto the rate determining step. In case of NiTet reaction it is proposed that in the pH range 5.0-8.0 NiTet and NiHTet are reactants as well as HCN and the experimental data are found to follow this proposition. In case of NiDien reaction, inverse first order dependence in hydrogen ion concentration suggests that one of the equilibria exists as $([\text{HCN}] \rightleftharpoons [\text{H}^+] + [\text{CN}^-])$. Since it is known from the species distribution that at pH 5 most of the Tet will be in the form of TetH_3^{3+} and Dien will be in the form of dienH_2^{2+} it is necessary to bring HCN in the fourth step to take care of stoichiometry, so the overall reaction will consume two HCN and two cyanides in the complete reaction. This view gets further support when one considers Margerum's work³⁵ where he too has assumed that two HCN and two cyanides are reactants around pH 5. A mechanistic scheme consistent with these

observations leads us to postulate that the mechanism for the two reactions are as follows:

For NiTet-CN⁻ reaction:



For NiDien-CN⁻ reaction:



For the sake of simplification coordinated water molecules have not been shown. The observation that there is no effect of ionic strength shows that one or both reacting species in the rate determining step should bear no charge. One of this species could be, therefore, HCN. The above proposition was also strongly supported by good agreement in the values of the stability constants of $\text{NiP}(\text{CN})_2$ intermediates calculated from the kinetic data and the spectrophotometric method (not shown).

A steady state treatment on the intermediate $\text{NiP}(\text{CN})_3$ in the postulated mechanism (as in the case of aminocarboxylate, Chapter II) gives the same rate law as observed experimentally.

In accord with the mechanism given above the forward reaction with first order dependence gives k_3 , that with second order give $K_2 k_3$ and third order gives $K_1 K_2 k_3$. We have, in both reactions, observed first order dependence only, though both first and second order was observed in some of our previous studies^{28,29,31} with some aminocarboxylates (Chapter II) and third to first order dependence were observed in the cases of NTA and EDDA.²⁷

A small algebraic manipulation gives the product $K_1 K_2 k_3$ in terms of known stability constants and protonation constants of reacting species.

$$K_1 K_2 k_3 = \frac{K_4^{-1} k_{-3} \beta_4 \cdot K_{\text{HCN}}^2}{K_{\text{H}_1} \cdot K_{\text{H}_2} \cdot K_{\text{H}_3} \cdot K_{\text{NiHTe}}^{\text{NiTe}} \cdot K_{\text{NiTet}}} \quad \dots (28)$$

where β_4 is the stability constant of $\text{Ni}(\text{CN})_4^{2-}$, K_{H_1} , K_{H_2} , K_{H_3} are the first, second & third dissociation constants of Tet.

$K_{\text{NiHTe}}^{\text{NiTet}}$ and K_{NiTet} are the protonation and the formation constants respectively of NiTet complex. Similarly, an expression for reaction of NiDien^{2+} with cyanide can be derived as:

$$K_1 K_2 k_3 = \frac{K_4^{-1} k_{-3} \beta_4 \cdot K_{\text{HCN}}^2}{K_{\text{H}_1} \cdot K_{\text{H}_2} \cdot K_{\text{NiDien}}} \quad \dots (29)$$

where K_{H_1} and K_{H_2} are the first and second dissociation constants respectively of Dien and K_{NiDien} is the formation constant of NiDien complex.

The work of Margerum et al.^{3,17} and X-ray crystal structure determination of $Ni(Dien)_2^{2+}$ by Biagini and Cannas⁵⁷ and work of Brackenridge⁵⁸ gave some clues to the postulated behaviour of the systems under investigation. Melson and Wilkins² in their investigation of acid dissociation of NiP^{2+} complexes showed that bonds of terminal amino groups of polyamines are in a greater state of strain and hence are comparatively easily unbound from the central Ni^{2+} ion in the initial stage of unwrapping process. The same may hold good during a ligand exchange reaction. Accordingly, the first cyanide may rapidly displace one of the weakly bound water molecules. The second cyanide would displace one of the terminal amino groups and this must also be a fast step. The third cyanide (or HCN) would displace the middle nitrogen atom which is bonded rather strongly. This step should be slow as a consequence. The fourth CN^- (or HCN) displaces the remaining labile segment in a fast step forming $Ni(CN)_4^{2-}$ and the free ligand (or its protonated forms depending upon the pH of the medium)*. The resolution of forward rate constants into terms due to CN^- and HCN shows that CN^- is a more reactive species compared to HCN. This accounts for the lowering of reaction rate at lower pH. Similar resolution shows that higher protonated forms of both polyamines are less reactive than less protonated forms.

*The same mechanism can be extended to $NiTet^{2+}$ reaction.

Like the aminocarboxylato nickel(II) reactions the activation parameters were also taken into consideration and the values support the contention that the reactions proceed through an associative mechanism rather than a dissociative one.⁵⁹

Our results are somewhat at variance with the results of Margerum et al.³⁵ They had observed a fourth order kinetics with respect to cyanide ions ^{for NiThien - CN⁻ reaction.} They had also observed first order dependence in each of reactants in the reverse reaction. We failed to see such dependence in our studies. It may be noted, however, that one of the conditions viz., pH was very different in their case (>9.0). In our case we did not observe the formation of a bridged complex as postulated in case of Ni(dien)EDTA reaction¹⁹ and some other exchange reactions.⁶⁰⁻⁶³

The values of rate constants and stability constants obtained from the present work are given in Table IV.6.

Table IV.6. Summary of rate constants and stability constants for NiP^{2+} reactions with CN^- at temp = $25 \pm 0.1^\circ\text{C}$; pH = 5.0; $\mu = 0.1 \text{ M}$

	NiTet	NiDien
$k_3, \text{M}^{-1}\text{S}^{-1}$	(1.52 ± 0.09)	(2.35 ± 0.05)
$k_4^{-1}k_{-3}, \text{S}^{-1}$	$(1.30 \pm 0.07) \times 10^{-4}$	$(0.24 \pm 0.04) \times 10^{-4}$
$k_{\text{CN}}, \text{M}^{-1}\text{S}^{-1}$	260	1.20×10^4
$k_{\text{HCN}}, \text{M}^{-1}\text{S}^{-1}$	1.52	0.07
$k_{\text{HP}}, \text{S}^{-1}$		2.02
$k_{\text{H}_2\text{P}}, \text{S}^{-1}$	0.10	6.0×10^{-6}
$k_{\text{H}_3\text{P}}, \text{S}^{-1}$	1.01×10^{-5}	

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CHAPTER V

MULTIDENTATE LIGAND KINETICS: THE EXCHANGE OF AMINOCARBOXYLATE IONS WITH TETRAETHYLENE PENTAMINE Ni(II)

ABSTRACT

In the present chapter the kinetics and mechanism of the following reaction is reported:



where Tet represents tetraethylene pentamine and L is HEEDTA (hydroxyethyl ethylenediamine triacetic acid) or TMDTA (trimethylenediamine tetraacetic acid). The reaction conditions are: temp = $25 \pm 0.1^\circ\text{C}$; $\mu = 0.1 \text{ M}$ (NaClO_4) and pH = 5 to 11. The reaction was followed by the cyanide quenching method. The displacement of Tet from its nickel(II) complex by aminocarboxylates is several orders of magnitude faster than aqueous dissociation of this complex in this pH range. The reaction is found to be first order in NiTet as well as in aminocarboxylate. The second order rate constants were estimated by the initial rate method and confirmed by the integrated second order rate plots. The effect of pH on both reactions has been investigated

and the activation parameters have been calculated. A reaction mechanism is proposed involving formation of a series of mixed ligand complex intermediates in which steric effect prevents full chelation of the six coordination sites of nickel ion by the two exchanging multidentate ligands and the coordinated water plays an important role.

V.1 Introduction

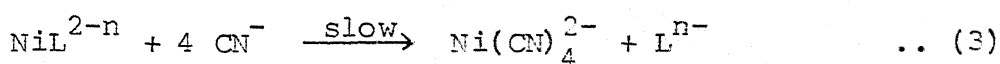
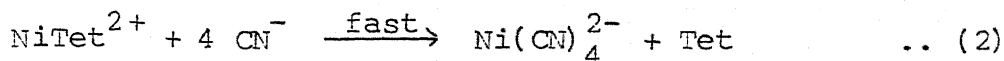
The mechanism by which one multidentate ligand displaces another from a metal ion depends upon the ability of both ligands to coordinate with the metal ion simultaneously. Interest in the relationship between substitution rates and water exchange rates on transition metal ions has been wide spread¹ in the last two decades. For the substitution of monodentate ligands on aquated nickel(II) ion a direct relationship appears to exist between these two processes.² Some investigators³⁻⁵ have applied this observation to account for enhanced reactivities which are observed when nonlabile ligands are coordinated to nickel(II). Although the extension of this simple relationship is appealing, it has been shown that marked increase in ligand substitution rate^{4,6} is not necessarily accompanied by a significant change in water exchange rate⁷ in the metal ion complex.

The nickel polyamine formation and dissociation reactions have been rather thoroughly studied.⁸⁻¹² The dissociation involves the following two steps repeated sequentially:¹⁰

methods previously reported.¹⁰ TMDTA was prepared by a method described in Chapter II and was recrystallised twice from ethanol-water mixture. HEEDTA was obtained from K & K Labs. (U.S.A.). All other solutions used were prepared as described in Chapters II to IV. The ionic strength was maintained at 0.1 M with NaClO_4 . All absorption measurements were made with a Toshniwal spectrophotometer model RL-02 which was equipped with a thermostated cell compartment. The reaction was followed by a cyanide quenching method which is described below:

CYANIDE QUENCHING METHOD

A method for quenching the reaction at suitable intervals by addition of cyanide was developed on the basis of a large difference in the rates of the reactions^{14, 15} (2) and (3):



It was found from our previous studies^{14, 15} that reaction (3) is very slow in comparison to reaction (2) with the concentration levels of cyanide added and the concentration of reactants and products present in the reaction mixture (0.5 - 1 mM NaCN and a maximum of 0.05 mM NiL^{2-n} at pH 11). Test runs showed that reaction (2) was complete within a few seconds under the same conditions. It was also tested that in presence of amino-carboxylates the reaction of NiTet and cyanide gives the product

$\text{Ni}(\text{CN})_4^{2-}$. Thus this method proved very effective in following the change in concentration of NiTet by its conversion to tetracyanonickelate, the absorbance of which was in turn measured at 267 nm ($\epsilon_{\text{Ni}(\text{CN})_4^{2-}} = 1.16 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) within five minutes of mixing. The concentration of $\text{Ni}(\text{CN})_4^{2-}$ thus determined gives the concentration of NiTet^{2+} . At this wavelength NiTet, NiTMDTA or NiHEEDTA do not absorb appreciably; their spectral peaks are NiTet: 380 nm, NiTMDTA: 360 & 560 nm and NiHEEDTA: 380 nm and 600 nm.

Protonation and Stability Constants and Species Distribution

The equilibrium constants for protonated tetren, nickel tetren complex, aminocarboxylates and aminocarboxylato Ni(II) complexes are listed in Table V.1. The species distribution at a particular pH was calculated by the method of Perrin and Sayce¹⁶ from the pK_a 's of complexes and ligands which are given in Table V.1.

Table V.1. Protonation constants of polyamine and aminocarboxylates and formation constants of their complexes with nickel(II)

A. Protonation Constants of Polyamine and Aminocarboxylates at 25°C and $\mu = 0.1 \text{ M}$.

L^{n-}	$\log K_{\text{HL}}$	$\log K_{\text{H}_2\text{L}}$	$\log K_{\text{H}_3\text{L}}$	$\log K_{\text{H}_4\text{L}}$	$\log K_{\text{H}_5\text{L}}$	Ref.
Tet	9.68	9.10	8.08	4.72	2.90	17
HEEDTA	9.81	5.41	2.72			18
TMDTA	10.27	7.90	2.67	2.0		19, 20

...contd.

Table V.1 (contd.)

B. Stability Constants and Protonation Constants of NiL Complexes at 25°C and $\mu = 0.1$ M

L^{n-}	$\log K_{NiL}^{Ni}$	$\log K_{NiHL}^{Ni}$	$\log K_{NiHL}^{NiL}$	$\log K_{NiH_2L}^{Ni}$	Ref.
Tet	17.43	11.78	4.93	6.7	17
HEEDTA	17.10		2.54 ^a		21
TMDTA	18.15	9.9			22

a, at $\mu = 1.25$ M.

The respective species distribution as a function of pH for Tet, NiTet, TMDTA and NiTMDTA and their respective protonated forms are given in Fig. IV.1 and Fig. II.7 while for HEEDTA and NiHEEDTA is given in Fig. V.1.

V.3 Results

Kinetics of Aminocarboxylate Exchange with NiTet

The rates of exchange of aminocarboxylate viz., TMDTA and HEEDTA with nickel tetren was studied from pH 5-11 using the cyanide quenching method. Both the reactions are thermodynamically favourable (stability constants in Table V.1).

The reaction orders were obtained from slopes of initial rate plots, determined by the plane mirror method.²³ A reaction order close to one for aminocarboxylates and also for NiTet complex (Table V.2 and Fig. V.2) was obtained from these data.

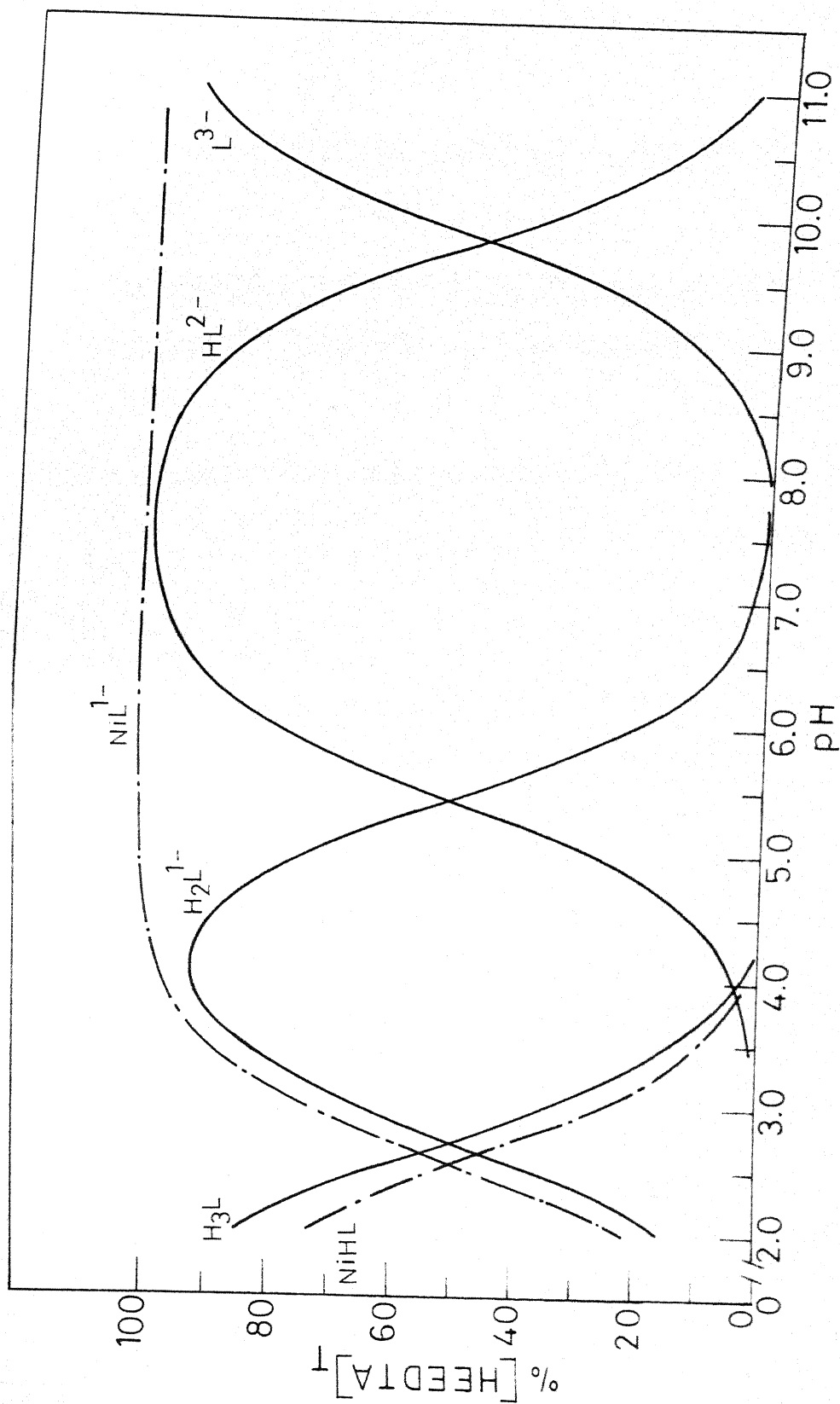


Fig. 2.1 Distribution of protonated and unprotonated forms of HEDTA and NiHEDTA^{1-} complex as a function of pH

Table V.2. Dependence of initial rates on the concentration of reactants

NiTet²⁺ - TMDTA System

(i) temp = 25±0.1°C; pH=11.0; and $\mu = 0.1$ M (NaClO₄)

$[\text{NiTet}^{2+}]$, M	$[\text{TMDTA}]$, M	Initial Rate, MS ⁻¹	k_L^{NiTet} , M ⁻¹ S ⁻¹
4.00 x 10 ⁻⁵	8.00 x 10 ⁻⁵	6.33 x 10 ⁻⁸	19.78
4.00 x 10 ⁻⁵	1.00 x 10 ⁻⁴	6.78 x 10 ⁻⁸	16.82
4.00 x 10 ⁻⁵	1.10 x 10 ⁻⁴	8.53 x 10 ⁻⁸	19.38
4.00 x 10 ⁻⁵	1.33 x 10 ⁻⁴	1.10 x 10 ⁻⁷	20.86
4.00 x 10 ⁻⁵	1.60 x 10 ⁻⁴	1.40 x 10 ⁻⁷	21.87
4.65 x 10 ⁻⁵	4.00 x 10 ⁻⁵	3.75 x 10 ⁻⁸	20.16
7.00 x 10 ⁻⁵	4.00 x 10 ⁻⁵	5.40 x 10 ⁻⁸	19.29
1.40 x 10 ⁻⁴	4.00 x 10 ⁻⁵	1.17 x 10 ⁻⁸	20.89

$$Av = (19.88 \pm 1.41)$$

(ii) temp = 25±0.1°C; pH = 5.5 and $\mu = 0.1$ M (NaClO₄)

4.00 x 10 ⁻⁵	4.00 x 10 ⁻⁵	1.00 x 10 ⁻⁷	62.50
4.00 x 10 ⁻⁵	4.44 x 10 ⁻⁵	1.08 x 10 ⁻⁷	60.81
4.00 x 10 ⁻⁵	5.00 x 10 ⁻⁵	1.35 x 10 ⁻⁷	67.50
4.00 x 10 ⁻⁵	5.70 x 10 ⁻⁵	1.54 x 10 ⁻⁷	67.54
4.00 x 10 ⁻⁵	6.65 x 10 ⁻⁵	1.75 x 10 ⁻⁷	65.78
4.00 x 10 ⁻⁵	8.00 x 10 ⁻⁵	2.00 x 10 ⁻⁷	62.50
4.45 x 10 ⁻⁵	4.00 x 10 ⁻⁵	7.47 x 10 ⁻⁸	41.97
5.00 x 10 ⁻⁵	4.00 x 10 ⁻⁵	8.18 x 10 ⁻⁸	40.90
5.71 x 10 ⁻⁵	4.00 x 10 ⁻⁵	1.03 x 10 ⁻⁷	45.10
6.67 x 10 ⁻⁵	4.00 x 10 ⁻⁵	1.15 x 10 ⁻⁷	43.10

..contd.

Table V.2 (contd.)

8.00×10^{-5}	4.00×10^{-5}	1.35×10^{-7}	42.18
			$\text{Av} = (54.53 \pm 11.0)$

NiTet²⁺-HEEDTA System

temp = $25 \pm 0.1^\circ\text{C}$; pH = 11.0; and $\mu = 0.10 \text{ M (NaClO}_4\text{)}$

$[\text{NiTet}^{2+}], \text{M}$	$[\text{HEEDTA}], \text{M}$	Initial Rate, MS^{-1}	$k_L^{\text{NiTet}}, \text{M}^{-1}\text{S}^{-1}$
4.00×10^{-5}	4.00×10^{-5}	1.16×10^{-8}	7.25
4.00×10^{-5}	5.70×10^{-5}	1.55×10^{-8}	6.81
4.00×10^{-5}	6.65×10^{-5}	2.52×10^{-8}	9.47
4.00×10^{-5}	8.00×10^{-5}	2.95×10^{-8}	9.24
4.00×10^{-5}	1.00×10^{-4}	3.49×10^{-8}	8.75
5.00×10^{-5}	4.00×10^{-5}	2.10×10^{-8}	10.50
5.70×10^{-5}	4.00×10^{-5}	2.27×10^{-8}	9.90
6.67×10^{-5}	4.00×10^{-5}	2.40×10^{-8}	9.00
			$\text{Av} = (8.87 \pm 1.10)$

The values of rate constants, k_L^{NiTet} , calculated by the initial rate method were checked with those obtained from the integrated rate plots. The rate expression can be written as

$$R_e = -d[\text{NiTet}]_T / dt = k_L^{\text{NiTet}} [\text{L}_T] [\text{NiTet}]_T \quad \dots (4)$$

The second order rate plots were linear over 50% of the reaction and extrapolated through the theoretical intercept. A slight deviation for later points is due to the contribution from backward reaction.

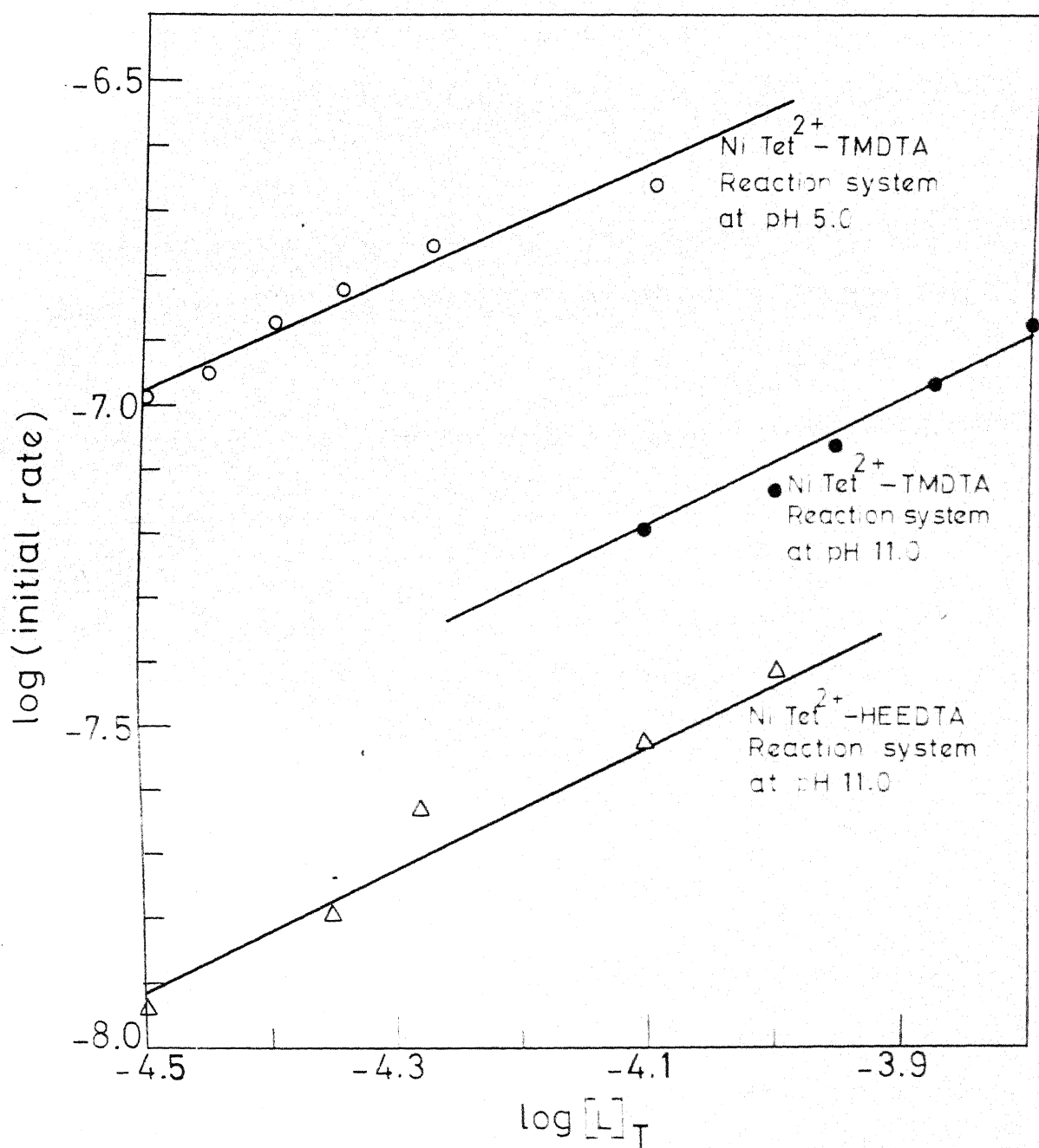


Fig. V.2 Order dependence in ligands for the reaction of Ni Tet^{2+} with amino-carboxylates

Effect of Temperature on the Rate of Reaction

Both reactions were carried out in a wide range of temperature and it was found that these reactions obey the Arrhenius equation (Fig. V.3). The activation parameters were calculated from these plots and are given in Table V.3.

Table V.3. Effect of temperature on the reaction of amino-carboxylates with NiTet^{2+}

$$[\text{NiTet}^{2+}]_T = [\text{L}]_T = 4.0 \times 10^{-5} \text{ M; pH} = 11.0 \text{ and } \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

temp, $\pm 0.1^\circ\text{C}$	$10^8 v_i, \text{MS}^{-1}$	$k_L^{\text{NiTet}}, \text{M}^{-1}\text{S}^{-1}$	Kinetic Parameters
<u>L: TMDTA⁴⁻</u>			
25	3.10	19.10	E_a kcal; 5.47
35	3.90	24.38	ΔH^\ddagger kcal; 4.28
40	4.79	29.94	ΔS^\ddagger e.u.; -34.11
45	5.50	34.37	$pZ \text{ cm}^{-1}$; 2.06×10^5
<u>L: HEEDTA³⁻</u>			
25	1.33	10.50	E_a kcal; 11.90
30	2.80	17.20	ΔH^\ddagger kcal; 11.31
35	4.08	25.66	ΔS^\ddagger e.u.; -15.66
40	4.62	28.87	$pZ \text{ cm}^{-1}$; 2.22×10^9
45	5.55	34.69	

Effect of pH on the Rate of Reaction

The data in Table V.4 and Fig. V.4 show that between pH 5 to 11.5 the reaction is strongly dependent on pH. The observed

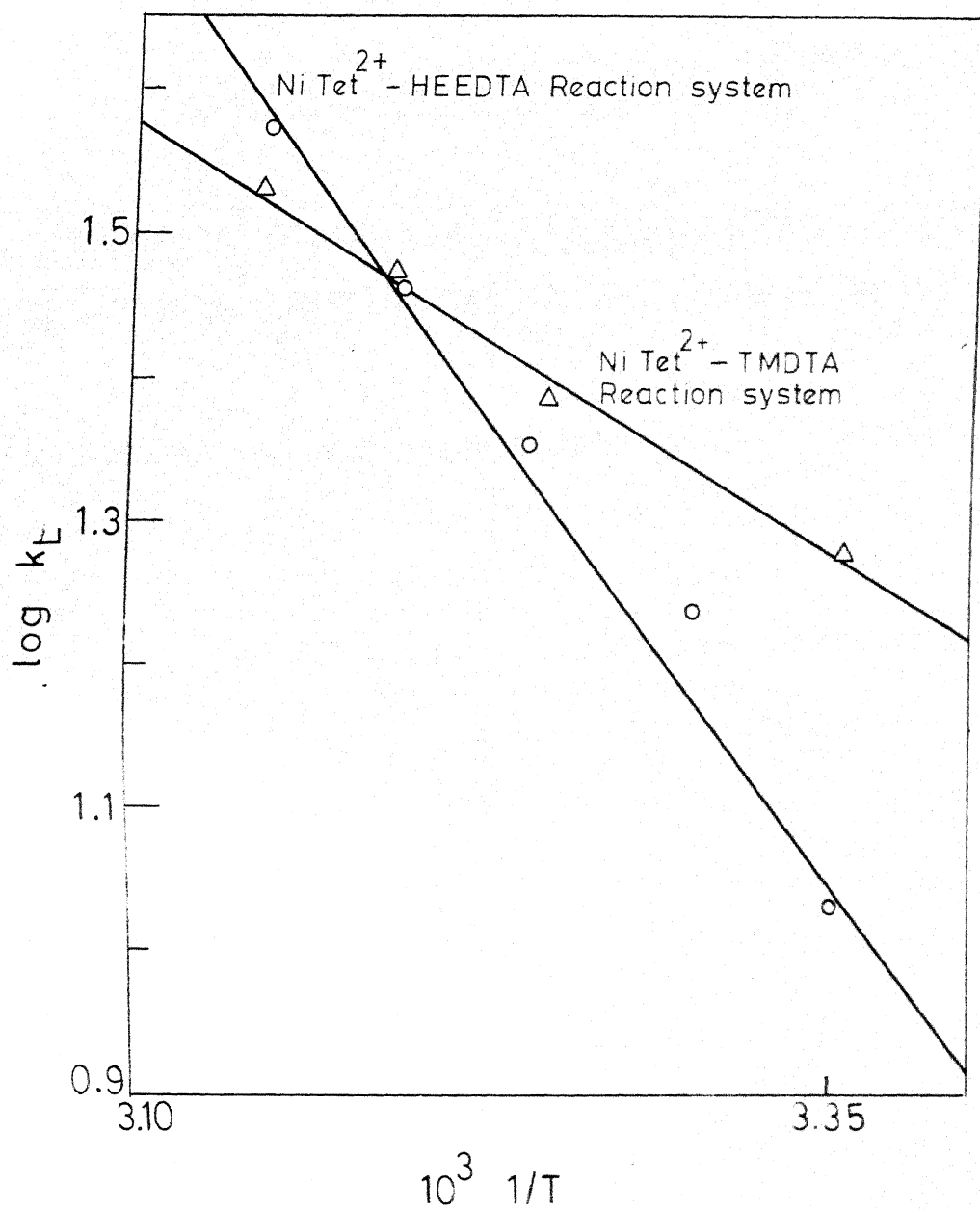


Fig. 2.3 Effect of Temperature on the Reaction of Ni Tet^{2+} with α -Aminoacrylates

Table V.4. Effect of pH on the rate of exchange of amino-carboxylates with NiTet^{2+}

$$[\text{L}]_{\text{T}} = [\text{NiTet}]_{\text{T}} = 4.0 \times 10^{-5} \text{ M; temp.} = 25^{\circ}\text{C; } \mu = 0.1 \text{ M (NaClO}_4\text{)}$$

pH	v_i, MS^{-1}	$k_{\text{LT}}^{\text{NiTet}}, \text{M}^{-1}\text{S}^{-1}$
<u>L: TMDTA⁴⁻</u>		
5.0	2.10×10^{-7}	130.00
5.5	7.03×10^{-8}	43.95
5.7	5.17×10^{-8}	32.33
6.5	2.63×10^{-8}	16.48
7.0	1.72×10^{-8}	10.78
7.5	1.09×10^{-8}	6.81
8.0	8.62×10^{-9}	5.39
9.0	1.40×10^{-8}	8.78
10.0	2.10×10^{-8}	13.69
10.5	3.00×10^{-8}	18.70
11.0	2.20×10^{-8}	14.21
<u>L: HEEDTA³⁻</u>		
5.5	8.08×10^{-8}	50.51
6.0	6.82×10^{-8}	42.65
6.5	5.02×10^{-8}	31.37
7.0	4.39×10^{-8}	27.43
7.5	2.87×10^{-8}	17.96
8.0	1.83×10^{-8}	11.49

...contd.

Table V.4 (contd.)

8.5	1.86×10^{-8}	11.65
9.0	1.91×10^{-8}	11.97
9.5	1.79×10^{-8}	11.22
10.0	1.61×10^{-8}	10.10
10.5	1.47×10^{-8}	9.22
11.0	1.40×10^{-8}	8.75

dependence can be attributed to the formation of various protonated and unprotonated forms of reactants. A pH less than 5 was not possible because of rapidity of the reaction and also because the species distribution may change considerably.

On the basis of acid dissociation constants for the aminocarboxylates and NiTet the following rate equation is proposed

$$R_e = \left\{ k_L [L^{n-}] + k_{HL} [HL^{1-n}] + k_{H_2L} [H_2L^{2-n}] + \dots \right\} \left\{ [NiTet] + [NiHTet] \right\} \quad \dots (5)$$

At pH 4.5 NiTet distribution is negligible.

In the working pH range, the terms in the first bracket involving more than two protons can be neglected. Therefore,

$$R_e = \left\{ k_L + k_{HL} K_1 [H^+] + k_{H_2L} K_1 K_2 [H^+]^2 \right\} \left\{ 1 + K_{NiHTet} [H^+] \right\} \times \left\{ [NiTet] [L^{n-}] \right\} \quad \dots (6)$$

where K_1 and K_2 are the first and second protonation constants of the aminocarboxylates and K_{NiHTet} is the protonation constant of NiTet. Multiplication of the first two brackets gives

$$R_e = \{k_L + k_{\text{HL}}[\text{H}^+] + k_{\text{H}_2\text{L}} K_1 K_2 [\text{H}^+]^2 + k_L K_{\text{NiHTet}} [\text{H}^+] + k_{\text{HL}} K_1 K_{\text{NiHTet}} [\text{H}^+]^2 + k_{\text{H}_2\text{L}} K_1 K_2 K_{\text{NiHTet}} [\text{H}^+]^3\} [\text{NiTet}] \cdot [\text{L}^{\text{n}}] \quad \dots (7)$$

or,

$$R_e = \{k_L + (k_{\text{HL}} K_1 + k_L K_{\text{NiHTet}}) [\text{H}^+] + (k_{\text{H}_2\text{L}} K_1 K_2 + k_{\text{HL}} K_1 K_{\text{NiHTet}}) [\text{H}^+]^2 + k_{\text{H}_2\text{L}} K_1 K_2 K_{\text{NiHTet}} [\text{H}^+]^3\} [\text{NiTet}] [\text{L}^{\text{n}}] \quad \dots (8)$$

$$= \{k_0 + k_1 [\text{H}^+] + k_2 [\text{H}^+]^2 + k_3 [\text{H}^+]^3\} [\text{NiTet}] [\text{L}^{\text{n}}] \quad \dots (9)$$

where the new rate constants k_0 to k_3 are collection of constants in Eqn. (8). Comparing Equations (4) and (9) one gets,

$$k_{\text{LT}} \frac{[\text{L}]_{\text{T}} [\text{NiTet}]_{\text{T}}}{[\text{L}^{\text{n}}]_{\text{T}} [\text{NiTet}]} = k_0 + k_1 [\text{H}^+] + k_2 [\text{H}^+]^2 + k_3 [\text{H}^+]^3 \quad \dots (10)$$

$$\text{where } \frac{[\text{L}]_{\text{T}}}{[\text{L}^{\text{n}}]_{\text{T}}} = 1 + K_1 [\text{H}^+] + K_1 K_2 [\text{H}^+]^2 + K_1 K_2 K_3 [\text{H}^+]^3 + \dots \dots (11)$$

K_1, K_2, K_3 etc. are protonation constants of the ligands and

$$\frac{[\text{NiTet}]_{\text{T}}}{[\text{NiTet}]} = 1 + K_{\text{NiHTet}} [\text{H}^+] \quad (K_{\text{NiHTet}} \text{ being the protonation constant of NiTet}).$$

These relationships have been listed to evaluate the concentration quotient on left hand side of Equation (10). The plot of $\log k_{LT}$ versus pH is shown in Fig. V.4.

A look at the Figs. II.7 and V.1 for TMDTA and HEEDTA would reveal that in the pH range 8.5-11.0 HL^{1-n} and L^{n-} are the principal species in solution. Considering these facts Eqn. (5) combined with Eqn. (4) followed by simple algebraic manipulation takes the form

$$k_{LT} \frac{[L]_T [NiTet]_T}{[L^{n-}] [NiTet]} = k_L + k_{HL} K_1 [H^+] \quad \dots (11)$$

The plots of left hand side of Eqn.(11) versus $[H^+]$ give

$$\begin{aligned} k_L &= \text{intercept} = 18.2 \text{ M}^{-1} \text{S}^{-1} \text{ for TMDTA reaction} \\ &= \text{intercept} = 8.10 \text{ M}^{-1} \text{S}^{-1} \text{ for HEEDTA reaction} \end{aligned}$$

$$\begin{aligned} k_{HL} K_1 &= \text{slope} = 1.66 \times 10^{11} \text{ M}^{-2} \text{S}^{-1} \text{ for TMDTA reaction} \\ &= 6.79 \times 10^{10} \text{ M}^{-2} \text{S}^{-1} \text{ for HEEDTA reaction} \end{aligned}$$

$$\begin{aligned} \text{and } k_{HL} &= \text{slope}/K_1 = 8.91 \text{ M}^{-1} \text{S}^{-1} \text{ for TMDTA reaction} \\ &= 12.64 \text{ M}^{-1} \text{S}^{-1} \text{ for HEEDTA reaction} \end{aligned}$$

In the pH range 5.5-8.0 the terms including one and two protons on the ligand are important and the protonated form of NiTet complex also plays an important role in the reaction. Equation (10) can be simplified into the following form,

$$A - (k_O + k_1 [H^+]) = k_2 [H^+]^2 + k_3 [H^+]^3 \quad \dots (12)$$

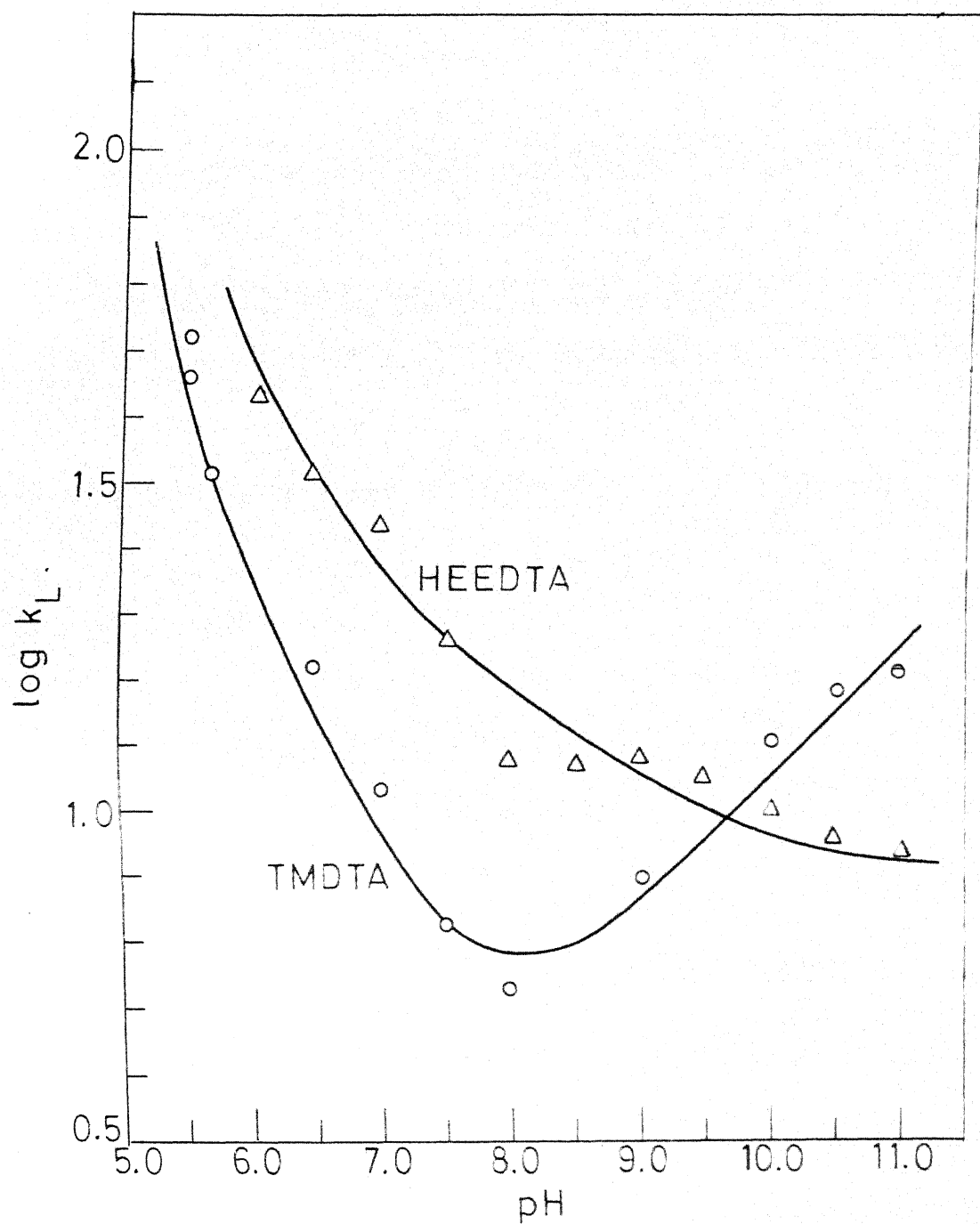


Fig. 3.4 Fit of Theoretical Curves and the Observed Rate Constants for Exchange of Aminocarboxylates with $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

$$\text{or } \{A - (k_0 + k_1[H^+])\} 1/[H^+]^2 = k_2 + k_3[H^+] \quad \dots (13)$$

where A is the left hand side of Eqn. (10). The plot of left hand side of Eqn. (13) versus $[H^+]$ gives the values of rate constant k_3 from which k_{H_2L} can be obtained (see Eqns. (8) and (9)):

$$\begin{aligned} k_{H_2L} &= 142.0 \text{ M}^{-1}\text{S}^{-1} \text{ for TMDTA} \\ &= 6.29 \times 10^3 \text{ M}^{-1}\text{S}^{-1} \text{ for HEEDTA} \end{aligned}$$

The protons can be assigned to reacting species in several ways. The alternate assignments of protons with the corresponding values of rate constants for each assignment are listed in Table V.5.

Table V.5. Evaluated rate constants^a with alternate assignment of protons at 25°C; $\mu = 0.1 \text{ M}$

NiTet + TMDTA

$k_L^{\text{NiTet}} = 18.2$	$k_L^{\text{NiHTet}} = 2.13 \times 10^7$	$k_L^{\text{NiH}_2\text{Tet}} = 2.79 \times 10^9$
$k_{HL}^{\text{NiTet}} = 8.91$	$k_{HL}^{\text{NiHTet}} = 1.04 \times 10^5$	$k_{HL}^{\text{NiH}_2\text{Tet}} = 1.65 \times 10^8$
$k_{H_2L}^{\text{NiTet}} = 142.0$	$k_{H_2L}^{\text{NiHTet}} = 1.66 \times 10^4$	

NiTet + HEEDTA

$k_L^{\text{NiTet}} = 8.10$	$k_L^{\text{NiHTet}} = 9.51 \times 10^6$	$k_L^{\text{NiH}_2\text{Tet}} = 1.50 \times 10^{10}$
$k_{HL}^{\text{NiTet}} = 12.64$	$k_{HL}^{\text{NiHTet}} = 1.49 \times 10^5$	$k_{HL}^{\text{NiH}_2\text{Tet}} = 2.35 \times 10^8$
$k_{H_2L}^{\text{NiTet}} = 6.29 \times 10^3$		

a, All rate constants in $\text{M}^{-1}\text{S}^{-1}$.

V.4 Discussion

Previous work¹⁰ has shown that the rate of dissociation of NiTet is much slower than the exchange rate of EDTA with this complex. Therefore, presence of the aminocarboxylate facilitates the dissociation of tetren from the coordination sphere of Ni^{2+} ion. The study of formation and dissociation of NiTet complex¹⁰ showed that both the processes take place through a succession of bond formation and bond rupture steps. The same appears to hold good in the reactions under investigation. It is proposed, as was done by Margerum et al.,³¹ that the entering aminocarboxylate forms coordinate bonds with Ni^{2+} ion prior to complete dissociation of nickel-polyamine bond. In this way the aminocarboxylates viz., TMDTA and HEEDTA block the reformation of nickel-polyamine bond much in the same manner as protons in the dissociation reactions. A series of mixed ligand complexes is formed in the intervening steps such that the coordination of nickel ion decreases with the polyamine and successively increases with the aminocarboxylate in each following step. The formation of such mixed ligand complexes is not unusual and has, in fact, been demonstrated^{25, 26} in many reactions involving displacement of polydentate ligands from their complexes.

A consideration of the peculiar structural features of EDTA and structurally similar aminocarboxylates would show that during formation of the first bond a carboxylate donor group is highly favoured over a nitrogen due to their steric configuration.

and the difficulty that the nitrogen atom experiences in approaching the coordination sites. The electrostatic attraction between Ni^{2+} and the COO^- should increase this preference further. When one considers the formation of second and subsequent bonds, the factors like steric difficulties and rotational barriers to be encountered for approaching the coordination sites on Ni^{2+} exclude the possibility that an aminocarboxylate atom can approach the nickel at the same time as a nickel-polyamine bond is being broken. On the other hand, the solvent molecules, in this case water, can rapidly coordinate at the site vacated by a polyamine segment. It is, therefore, proposed that the mechanism of displacement of a polyamine by an aminocarboxylate consists of two alternating steps—a cleavage of a nickel-polyamine bond attended by rapid coordination by the water molecules at the vacated site followed by rupture of the nickel-water bond and rapid coordination of the aminocarboxylate donor atom, which must rotate to assume a position favourable for bonding.

These features of the mechanism proposed above are presented in Fig. V.5. Here the reaction of non-protonated reactants has been depicted. To the best of our knowledge the detailed structure of NiTet complex is not known. We have assumed that its structure is similar to the structure of CuTet given in the literature²⁹ in which tetren is pentacoordinated and the sixth site is occupied by a water molecule. A structure shown in Fig. V.5 (I) has been taken as the starting point for elucidation of the suggested mechanism.

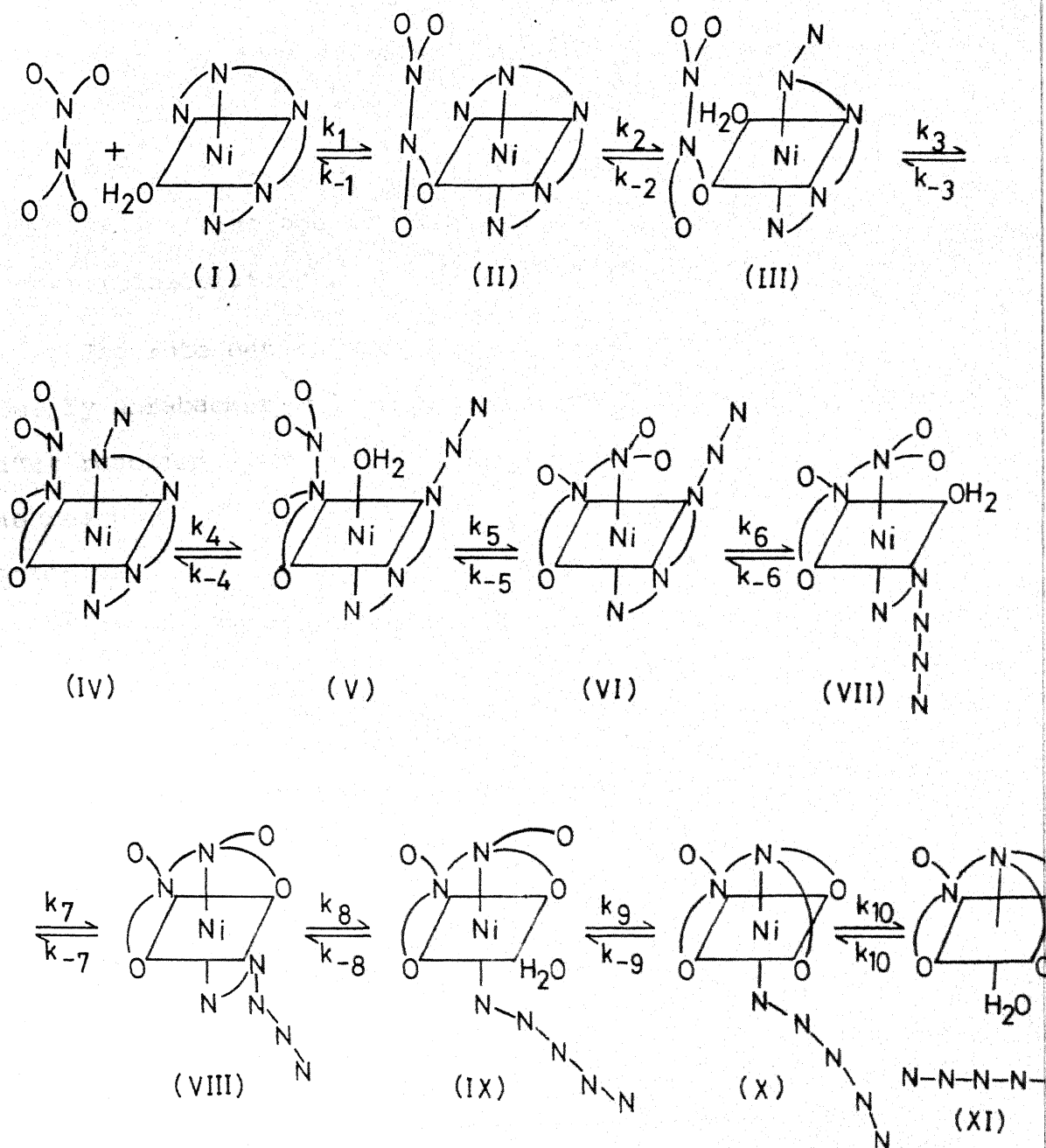


Fig. V.5 Proposed Mechanism for Aminocarbonylate Exchange with NiTet^{2-}

The pin pointing of the rate determining step poses a difficult problem but this should be one of the two following processes: (a) loss of water³⁰ or (b) the rupture of metal-polyamine bond. It should thus depend upon either the rate constant for water loss (similar to metal chelate formation) or rate constant for breakage of nickel-polyamine bond (similar to metal chelate dissociation).

The rate determining step can be identified by a method used by Rorabacher and Margerum³¹ for the cases of NiTrien and NiTet reaction with EDTA or that used by Carr and Olson²⁹ for the reaction of CuTrien and CuDien with Tetren, or a third method used by Kodama et al.^{31a} for the reaction of EDTA and HEEDTA with NiEDMA and NiDien. We found the first method handy and made use of the same in this work. The basic idea is that the experimental rate constants can be equated to the relative stability of the intermediate immediately preceding the rate determining step by the following relationship:

$$k_{\text{exptl}} = \frac{K_{(\text{nth intermediate})}}{K_{\text{reactants}}} \cdot k_n \quad \dots (14)$$

where,

$$K_{(\text{nth intermediate})} = \frac{K_{\text{polyamine-segment}} \times K_{\text{aminocarboxylate-segment}}}{K_{\text{electrostatic}}}$$

and k_n is the rate constant for nickel-nitrogen or nickel-water bond breaking process corrected for rotational barrier involved in the particular case. This has been estimated³¹ to be close

to 80 s^{-1} for steps involving k_2, k_4, k_6 etc. all of which are characterised by the rupture of nickel-nitrogen bond and rotation about C-N or C-C bond. A value of $6.0 \times 10^2 \text{ s}^{-1}$ has been estimated for steps involving k_5, k_7 etc., while for step k_3 where preferred orientation is around C-O bond it is approximately $1.0 \times 10^4 \text{ s}^{-1}$. The other simplifying approximations³¹ used are:

$$K_{\text{polyamine segment}} = K_{\text{NiDien}}^{\text{Ni}} = 10^{10.7}$$

$$K_{\text{aminopolycarboxylate segment}} = K_{\text{Ni(OAc)}_2}^{\text{Ni}} = 10^{0.7}$$

$$K_{\text{electrostatic}} = 0.1.$$

Equation (14) can be used to check all possible mixed ligand complex intermediates shown in Fig. V.5 with the experimentally observed rate constants. Inserting appropriate values in the equation one gets,

$$\text{for } k_3; k_{\text{exptl.}} = \frac{10^{10.7} \times 10^{0.7} \times 10^4}{0.1 \times 10^{17.5}} = 10^{-1.1} = 7.9 \times 10^{-2}$$

$$\begin{aligned} \text{for } k_2, k_4, k_6 \text{ etc;} \quad k_{\text{exptl.}} &= \frac{10^{10.7} \times 10^{0.7} \times 80}{0.1 \times 10^{17.5}} \\ &= 8 \times 10^{-4.1} = 6.35 \times 10^{-4} \end{aligned}$$

$$\begin{aligned} \text{and for } k_5, k_7 \text{ etc.;} \quad k_{\text{exptl.}} &= \frac{10^{10.7} \times 10^{0.7} \times 6.10^2}{0.1 \times 10^{17.5}} \\ &= 6 \times 10^{-3.1} = 4.76 \times 10^{-3} \end{aligned}$$

These values should be matched with the experimentally observed rate constants. One can infer from the above set of calculations that the observed value of rate constant is close in case of k_3 than with other constants such as k_2 , k_4 , k_6 etc. or with k_5 , k_7 etc. Therefore, in all probability the rate determining step will be at k_3 .

The intermediate preceeding the rate determining step is characterised as having four nitrogens of tetren and one acetate of aminocarboxylate viz. TMDTA or EDTA coordinated to the nickel ion. The rate determining step appears to be the loss of a water molecule followed by coordination of the first nitrogen of TMDTA or HEEDTA.

If it is assumed that the Eigen mechanism³⁰ can be extended to this class of reactions (as has been done by previous investigators³⁸), the rate constants can be predicted from the values of K_{os} (outer sphere association constant) and k_{-H_2O} (the rate constant for water loss). For such systems the reaction intermediate preceeding the water loss is the "ion pair" and the value of association equilibrium constant K_{os} can be calculated from the equation derived by Fuoss³³ and used for similar reaction systems by Rorabacher³⁴ and Gordon et al.³⁸ (An equation has also been derived by Debye^{35,36} for calculating the outer sphere association constant but it was not used in this work). The Fuoss equation is written as

$$K_{os} = \frac{4}{3} \pi a^3 N_A \cdot e^b \times 10^{-3} \quad \dots (15)$$

$$\text{where } b = \frac{Z_A Z_B \cdot e_o^2}{a \cdot D \cdot kT} .$$

In the above expression, all the symbols have their usual meanings and 'a' denotes the centre to centre distance (cm) between the two reaction partners. Various values of 'a' have been used by different investigators in the reaction systems studied by them. For example, Gordon et al.³⁸ have used values between 3.5 to 5 Å for $\text{Ni}(\text{H}_2\text{O})_6$ reaction with some neutral ligands while Steinhaus and Boeserma³⁸ used a value of 3.5 Å for Nitrien reaction with phenanthroline. We have made use of a value of 6 Å based on reasonable estimates. Similarly we have used a value of $k^{-\text{H}_2\text{O}}$ equal to $2.7 \times 10^4 \text{ s}^{-1}$ determined for $\text{H}_2\text{O}-\text{H}_2\text{O}$ exchange³⁷ on Ni^{2+} . The value of water loss constant for $\text{Cu}(\text{en})_2$ -en exchange was estimated to be $1.2 \times 10^7 \text{ s}^{-1}$ & $1.99 \times 10^5 \text{ s}^{-1}$ for Ni-glutamate reaction with calmagite.³⁹ The values of rate constants calculated from the following equation:

$$k_{\text{exptl.}} = K_{\text{OS}} k^{-\text{H}_2\text{O}} \quad \dots (16)$$

with $a = 6 \text{ Å}$ and $k^{-\text{H}_2\text{O}} = 2.7 \times 10^4 \text{ s}^{-1}$ for reaction of non-protonated and protonated forms are tabulated and compared with experimental values in Table V.6. Considering the approximations involved in these calculations the agreement may be considered good.

A comparison of rate constants for some similar reactions will be in order. k_L values for NiTet-L exchange reactions, where L is EDTA,³¹ HEEDTA, TMDTA and TTHA¹³ are 1.5, 8.10,

Table V.6. Values of rate constants for the substitution reaction of nickel(II) polyamine by amino-carboxylates.

Experimental value	Predicted value
(i) <u>NiTet²⁺-TMDTA Reaction System</u>	
$k_L = 18.2 \text{ M}^{-1} \text{ S}^{-1}$	$k_L = 1.09 \text{ M}^{-1} \text{ S}^{-1}$
$k_{HL} = 8.91 \text{ M}^{-1} \text{ S}^{-1}$	$k_{HL} = 11.50 \text{ M}^{-1} \text{ S}^{-1}$
$k_{H_2L} = 142.0 \text{ M}^{-1} \text{ S}^{-1}$	$k_{H_2L} = 115.68 \text{ M}^{-1} \text{ S}^{-1}$
(ii) <u>NiTet²⁺-HEEDTA Reaction System</u>	
$k_L = 8.10 \text{ M}^{-1} \text{ S}^{-1}$	$k_L = 5.73 \text{ M}^{-1} \text{ S}^{-1}$
$k_{HL} = 12.64 \text{ M}^{-1} \text{ S}^{-1}$	$k_{HL} = 115.68 \text{ M}^{-1} \text{ S}^{-1}$
$k_{H_2L} = 6.29 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$	$k_{H_2L} = 1.35 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$

18.2 and $1.6 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$ respectively. According to Rorabacher and Margerum^{31a} an increasing number of similar donor atoms on the incoming ligand should increase the reaction rate. Because TTHA molecule has ten donor atoms, an increase in the reaction rate could be expected when EDTA is replaced by TTHA in the reaction with Ni(II) amine complex. A comparison between EDTA, HEEDTA and TMDTA reaction with NiTet can be made on the basis of the stability constants of their sodium complexes and their respective reactivities. It is observed in Chapter II that NaL^{3-} is less reactive in comparison to L^{4-} . The $\log K_{\text{NaL}}$ values are 1.69,⁴⁰ 1.30⁴¹ and 1.08⁴² for EDTA, HEEDTA and TMDTA respectively. The rate constants follow the reverse order.

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CHAPTER VI

DETERMINATION OF STABILITY CONSTANTS OF ALKALI METAL COMPLEXES OF AMINO CARBOXYLATES BY A KINETIC METHOD

ABSTRACT

A kinetic method is developed for the determination of stability constants for complexes of aminocarboxylates with alkali metal ions. The method is based on the effect of the concentration of these ions on the rate of reaction of $\text{Ni}(\text{CN})_4^{2-}$ with the respective aminocarboxylates. The reaction conditions are temp = $25 \pm 0.1^\circ\text{C}$; pH = 11.0 ± 0.1 and $\mu = 0.5$ M. The stability constants follow the general order $\text{LiL} > \text{NaL} > \text{KL} > \text{RbL} > \text{CsL}$.

VI.1 Introduction

Recently several reports have appeared on the formation of the weak 1:1 complexes between the alkali metal ions and the multidentate ligands viz. ethylenediamine-tetraacetic acid (EDTA),¹ 1,2-diaminopropane-tetraacetic acid (PDTA),²⁻⁴ trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (CyDTA),^{5,6}

2,3-diaminobutane-N,N,N',N'-tetraacetic acid (BDTA)⁷ and (ethyleneglycol)bis(2-aminoethyl ether)-N,N,N',N'-tetraacetic acid (EGTA)⁸ making use of various methods like potentiometry, sodium sensitive glass electrode, spectrophotometry, polarography and polarimetry. In the present work we have developed a kinetic method for the estimation of stability constants of alkali metal complexes of three aminocarboxylates viz., TMDTA, DTPA and TTHA though the method can be extended to other aminocarboxylates.

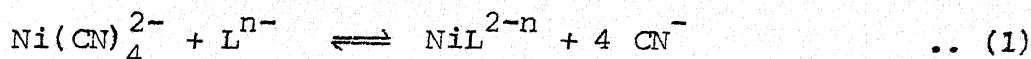
VI.2 Experimental Section

(A) Apparatus: The apparatus used is the same as described in Chapter II, viz. a spectrophotometer, a pH meter and a thermostatic bath etc.

(B) Reagents: All reagents used in this study were of AR grade. TMDTA was prepared by the method of Weyh and Hamm⁹ while DTPA and TTHA were obtained from Geigy Labs. (U.S.A.) and Sigma Chemicals, St. Louis (U.S.A.) respectively. AR grade tetramethyl ammonium chloride (TMACl) was used for maintaining ionic strength along with respective alkali metal salts.

$\text{Na}_2\text{Ni}(\text{CN})_4^{2-}$ was prepared as described in Chapter II.

(C) Background: In Chapter II a detailed kinetic study of the following reaction has been presented:



where L represents aminocarboxylates viz., 1,2-PDTA, DTPA, TMDTA or TTHA. It was pointed out therein and in one of our earlier communications¹⁰ that the rate of above reaction varies if one uses different supporting electrolytes (NaClO_4 or KNO_3) for ionic strength maintenance. This was shown to be due to the formation of the weak alkali metal complexes whose reactivities are different and, in general smaller as compared to aminocarboxylates. It was also demonstrated that the rate data of this reaction could be used for determination of the stability constants of NaL^{-n+1} complex.

Table VI.1 shows the pK_a values of TMDTA (tetramethylenediamine tetraacetic acid) in three different media viz., KNO_3 ,¹¹ $(\text{CH}_3)_4\text{NCl}$ ¹² and NaNO_3 .¹³ A look at these values would reveal that the dissociation of TMDTA is related to the presence of alkali metal ions.

These data can be used to estimate the stability constants of MTMDTA^{3-} where M is Na^+ or K^+ by the following procedure.

It is known that when a non-complexing agent such as TMACl is used as a medium,

$$K_{\text{HL}(\text{TMACl})} = \frac{[\text{H}^+][\text{L}^{4-}]}{[\text{HL}^{3-}]} \quad \dots (2)$$

Table VI.1. Acid dissociation constants of trimethylene-diamine tetraacetic acid in different media at temp = 25°C; $\mu = 0.1$ M.

Medium	pK ₄	pK ₃	pK ₂	pK ₁	Ref.
KNO ₃	10.46	8.02	2.5	1.90	11
(CH ₃) ₄ NCl	10.56	8.00	-	-	11
NaNO ₃	10.27	7.90	2.67	2.00	12, 13

The later part of the subscript is added to emphasize the role of the medium. But, in presence of a complexing ion

$$K_{HL(ML)} = \frac{[H^+] \{ [ML^{3-}] + [L^{4-}] \}}{[HL^{3-}]} \quad \dots (3)$$

where M⁺ may be a sodium or potassium ion. Equation (3) can be transformed into

$$\begin{aligned} K_{HL(ML)} &= \frac{[H^+] \{ K_{ML} [M^+] [L^{4-}] + [L^{4-}] \}}{[HL^{3-}]} \\ &= \frac{[H^+] [L^{4-}]}{[HL^{3-}]} \{ K_{ML} [M^+] + 1 \} \quad \dots (4) \end{aligned}$$

Substituting for the terms outside the bracket from Equation(2)

$$K_{HL(ML)} = K_{HL(TM\text{ACl})} \{ K_{ML} [M^+] + 1 \} \quad \dots (5)$$

$$\text{or} \quad K_{ML} [M^+] = \frac{K_{HL(ML)}}{K_{HL(TM\text{ACl})}} - 1$$

$$\text{or } K_{ML} = \frac{1}{[M^+]} \left\{ \frac{K_{HL(ML)}}{K_{HL(TM\text{ACl})}} - 1 \right\} \quad \dots (6)$$

Substituting appropriate values in this expression

$$K_{ML} = \frac{1}{0.1} \left\{ \frac{10^{-10.27}}{10^{-10.56}} - 1 \right\} = 9.50$$

(when M^+ is Na^+ ion.)

$$\text{and } K_{ML} = \frac{1}{0.1} \left\{ \frac{10^{-10.46}}{10^{-10.56}} - 1 \right\} = 2.59$$

(when M^+ is K^+ ion.)

These values give a rough estimate of the values to be expected from a more elaborate procedure to be discussed now.

(D) Procedure

The experimentation carried out for evaluation of stability constants consisted in measuring the rates of reaction (1) using a non-complexing agent tetramethyl ammonium chloride for ionic strength control ($\mu = 0.5 \text{ M}$) and tetramethyl ammonium hydroxide for pH maintenance ($\text{pH} = 11$) in presence of varying concentration (0-0.3 M) of alkali metal ions viz., Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ . A mathematical expression (to be derived later) was developed which could be used to correlate the measured rates with the stability constants of the respective alkali metals. The conditional rate constants of substitution reactions determined under these condition are given in Table VI.2

Table VI.2. Rate constants for decomposition of tetracyanonickelate in presence of aminocarboxylates (L) by using TMACl and alkali metals for maintaining ionic strength (0.5 M).

Reaction conditions are: temp = 25°C; $\mu = 0.5$ M;
pH = 11.0; $[\text{Ni}(\text{CN})_4^{2-}] = 6.60 \times 10^{-5}$ M.

Alkali Metal Concen- tration, M	$k_r = k_4^{-1} k_{-3} \text{ s}^{-1}$		
	TMDTA ⁴⁻ ^a	DTPA ⁵⁻ ^b	TTHA ⁶⁻ ^c
<u>Li⁺</u>			
0.0	4.65×10^{-7}	1.68×10^{-7}	4.48×10^{-7}
0.05	8.79×10^{-8}	1.08×10^{-7}	9.73×10^{-8}
0.10	4.59×10^{-8}	8.27×10^{-8}	6.45×10^{-8}
0.20	2.30×10^{-8}	2.98×10^{-8}	2.76×10^{-8}
0.30	1.49×10^{-8}	-	-
<u>Na⁺</u>			
0.0	4.65×10^{-7}	1.68×10^{-7}	4.48×10^{-7}
0.05	-	1.16×10^{-7}	2.67×10^{-7}
0.10	2.00×10^{-7}	9.42×10^{-8}	9.84×10^{-8}
0.20	8.60×10^{-8}	3.90×10^{-8}	7.37×10^{-8}
0.30	4.24×10^{-8}	3.05×10^{-8}	-
<u>K⁺</u>			
0.0	4.65×10^{-7}	1.68×10^{-7}	
0.05	3.40×10^{-7}	1.25×10^{-7}	
0.10	2.06×10^{-7}	9.88×10^{-8}	
0.20	1.15×10^{-7}	5.75×10^{-8}	
0.30	8.62×10^{-8}	3.91×10^{-8}	

..contd.

Table VI.2 (contd.)

Rb⁺

0.0	4.65×10^{-7}	1.68×10^{-7}	4.48×10^{-7}
0.05	4.40×10^{-7}	1.60×10^{-7}	3.68×10^{-7}
0.10	4.02×10^{-7}	1.45×10^{-7}	3.23×10^{-7}
0.20	3.16×10^{-7}	1.30×10^{-7}	2.94×10^{-7}
0.30	2.81×10^{-7}	1.23×10^{-7}	2.30×10^{-7}

Cs⁺

0.0	4.65×10^{-7}	4.48×10^{-7}
0.05	4.52×10^{-7}	4.16×10^{-7}
0.10	4.40×10^{-7}	4.00×10^{-7}
0.20	4.00×10^{-7}	3.69×10^{-7}
0.30	3.96×10^{-7}	3.60×10^{-7}

a, $[\text{TMDTA}^{4-}]_T = 2.5 \times 10^{-3} \text{ M}$; b, $[\text{DTPA}^{5-}]_T = 6.25 \times 10^{-3} \text{ M}$;
 c, $[\text{TTHA}^{6-}]_T = 3.12 \times 10^{-3} \text{ M}$.

DERIVATION

Denoting the conditional rate constants of substitution reaction by the uncomplexed ligand L^{4-} and the weak complex ML^{3-} by $k_{r(\text{L})}$ and $k_{r(\text{ML})}$ respectively and total ligand concentration by C_L we have,

$$k_{r(\text{L}, \text{ML})} \cdot C_L = k_{r(\text{L})} [\text{L}^{4-}] + k_{r(\text{ML})} [\text{ML}^{3-}] \quad \dots (7)$$

Since the alkali metal complex is very weak it can be assumed $[\text{NaL}^{3-}] \ll C_{M+}$, the total metal concentration. Hence

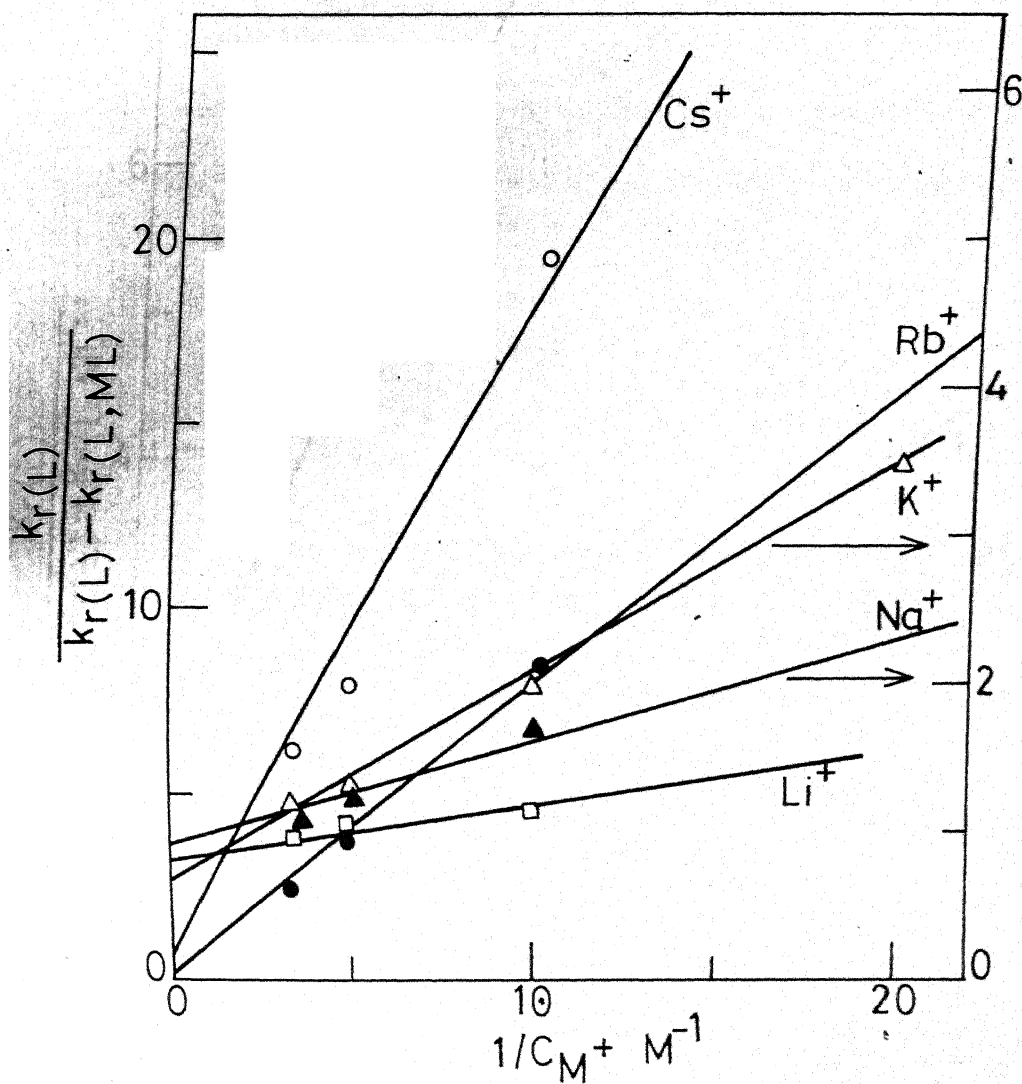


Fig. VI.1 Determination of Stability Constants of Alkali Metal Complexes of TMDTA

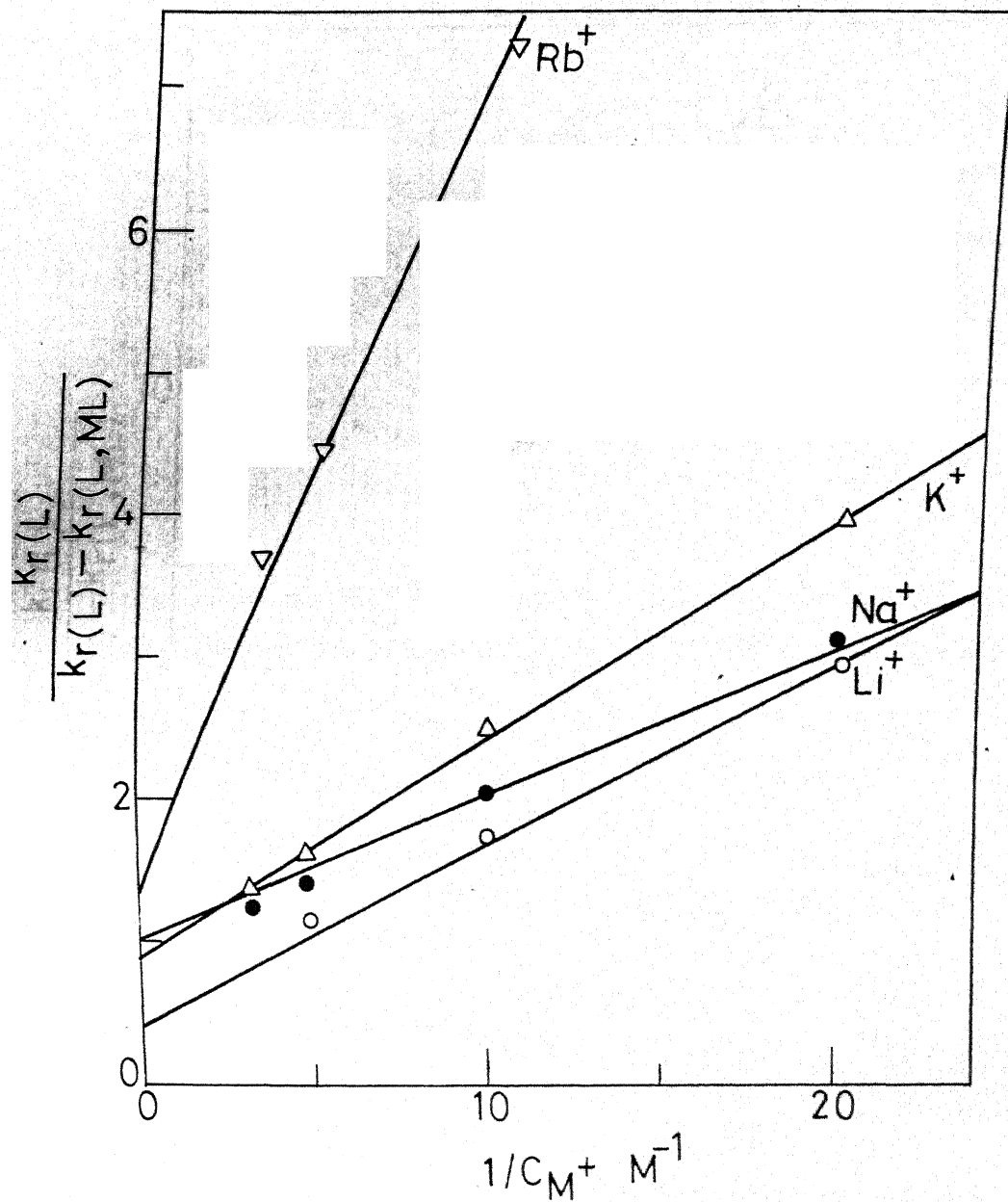


Fig. VI.2 Determination of Stability Constants of Alkali Metal Complexes with DTPA

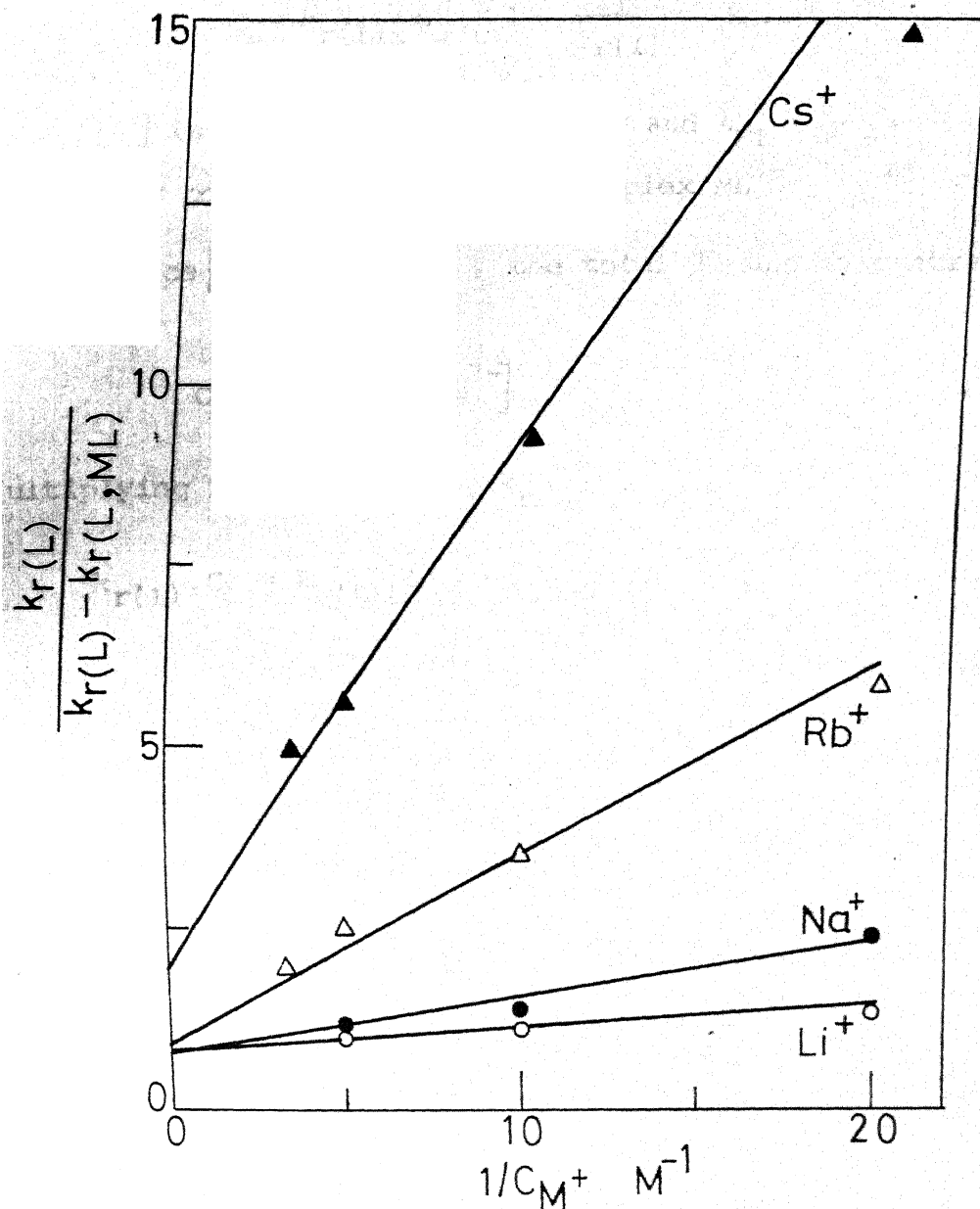


Fig. VI.2 Determination of Stability Constants of Alkali Metal Complexes of TTHA

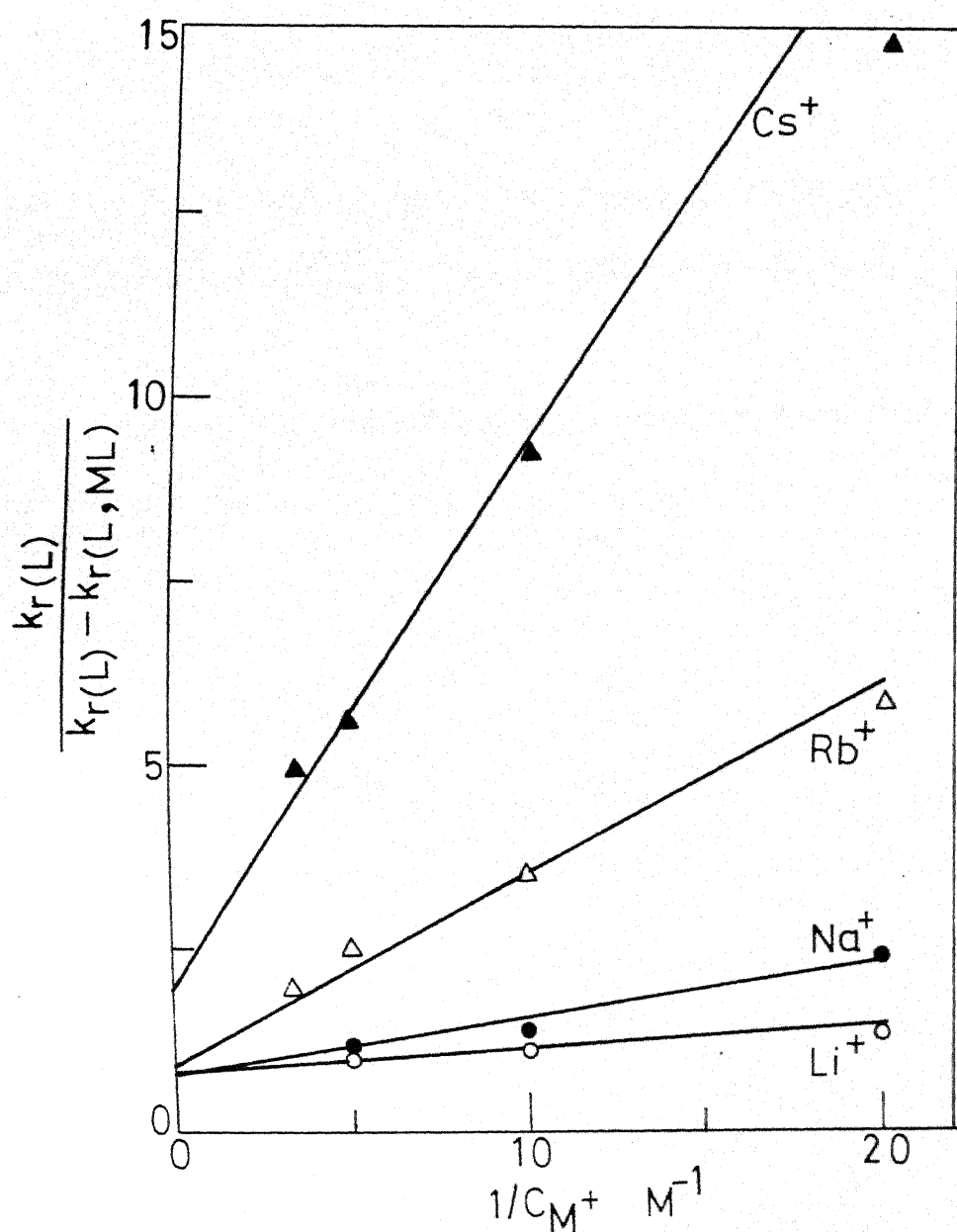


Fig. VI.3 Determination of Stability Constants of Alkali Metal Complexes of TTHA

$$\frac{k_{r(L)}}{k_{r(L)} - k_{r(L, ML)}} = \left\{ \frac{[L'] + [ML^{3-}]}{[ML^{3-}]} \right\} \frac{1}{\left\{ 1 - \frac{k_{r(ML)}}{k_{r(L)}} \right\}}$$

$$= \left\{ 1 - \frac{k_{r(ML)}}{k_{r(L)}} \right\}^{-1} \left\{ 1 + \frac{L'}{ML^{3-}} \right\} \dots (14)$$

Finally,

$$\frac{k_{r(L)}}{k_{r(L)} - k_{r(L, ML)}} = \left\{ 1 - \frac{k_{r(ML)}}{k_{r(L)}} \right\}^{-1} \left\{ 1 + \frac{1}{K_{ML} \cdot C_{M^+}} \right\} \dots (15)$$

A plot of $k_{r(L)} / k_{r(L)} - k_{r(L, ML)}$ versus the reciprocal of concentration of metal ion, $1/C_{M^+}$, should yield a straight line (Fig. VI.1 & VI.3) from the slopes of these straight lines K_{ML} may be obtained for each case. The results are compiled in Table VI.3.

VI.3 RESULTS AND DISCUSSION

The stability constants of alkali metal complexes of amino-carboxylates are relatively quite small compared to those of transition metal complexes of aminocarboxylates. The values of stability constants can be determined from the plots of Eqn.(15) (Fig. VI.1 to VI.3). The results given in Table VI.3 show some general trends. At high pH the stability constants follow the expected order $K_{LiL} > K_{NaL} > K_{KL} > K_{RbL} > K_{CsL}$. A similar order was observed by Carr et al. for alkali metal complexes of 1-PDTA⁴ and CyDTA⁵ and by Bott et al. for corresponding EDTA^{1c} complexes. A similar order was predicted, though, qualitatively for EDTA on the basis of NMR experiments by Kuala et al.¹⁴

Table VI.3. Stability constants of alkali metal complexes with aminocarboxylates at temp = 25°C ; $\mu = 0.5$ M ; and pH = 11.0.

L^{n-}	Stability Constants				
	LiL^{3-}	NaL^{3-}	KL^{3-}	RbL^{3-}	CsL^{3-}
TMDTA ⁴⁻	24.28	12.8	3.75	0.26	0.21
DTPA ⁵⁻	3.06	10.0	4.84	2.16	-
TTHA ⁶⁻	22.85	12.14	-	2.96	2.60
EDTA ⁴⁻	710 ^a	62 ^a	9.2 ^a	3.9 ^a	1.4 ^a
CDTA ⁴⁻	1.3x10 ^{6b}	4.6x10 ^{4b}	68 ^b	-	7.0 ^b
	1.35x10 ^{4c}	5.01x10 ^{2c}			
1,2-PDTA ⁴⁻	1.02x10 ^{4d}	3.56x10 ^{2d}	8.06 ^d	0.16 ^e	-
d-BDTA ^f	5.25 ^f	3.93 ^f	1.56 ^f	-	-
EGTA ⁴⁻	15 ^g	24 ^g	-	-	-

a, $\mu = 0.32$ M(CsCl), Ref. 1c; b, Ref. 5; c, Ref. 6; d, Ref. 4; e, Ref. 2; f, Ref. 7; g, Ref. 8.

A notable exception is the value of K_{LiL} for DTPA and EGTA.⁸ This is not entirely unexpected in view of the high charge/radius ratio and exceptional solvation of Li^+ , though it is difficult to explain why it follows the normal order in case of other aminocarboxylates listed in Table VI.3.

The dependence of stability constants of alkali metals on pH in cases of 1-PDTA⁴ and trans-CyDTA⁵ has received the

attention of Carr et al. (although the same has not been attempted in the present work). At low pH the order of stability constants is reverse and this has been attributed to the interaction of alkali metal ions with H_2L rather than L . From a comparison of pK_4 , $\log K_{LiL}$ and $\log K_{NaL}$ values for the structurally similar ligands viz. EDTA, 1-PDTA, dl-BDTA and trans-CyDTA Carr et al.⁷ demonstrated that a simple correlation exists between the proton affinities of these ligands and their affinities for these alkali metals. The value for TMDTA complexes also fits in the same pattern. This indicates that in case of Li^+ and Na^+ the free energy change accompanying the reaction



is unrelated to the identity of the ligand. It is also inferred that both HL^{3-} and ML^{3-} possess similar structural features.

It is appealing to speculate about the nature of interaction between alkali metal ions and the aminocarboxylates. The effect on chemical shift¹⁴ of methyl and methylene protons in EDTA suggested that the alkali metals are bonded to the nitrogen atoms in preference to the carboxylate group. It was also concluded from the averaged resonance signal that there exists a rapid exchange of metal ions between carboxylate group. In the net analysis the nature of interaction of alkali metal ions with carboxylate groups is quite weak. More work is planned to gain a better insight into these interactions.

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A P P E N D I X

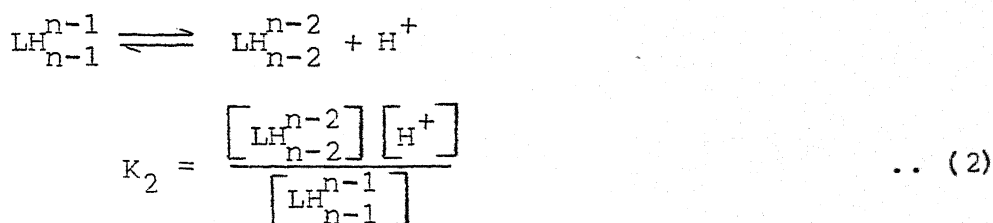
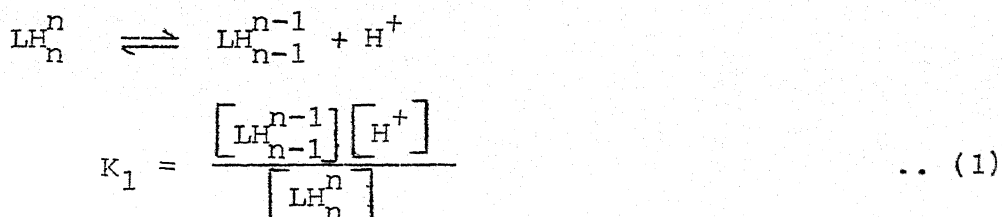
Introduction

For the kineticists it is very important to know the concentration of predominant reacting species. On this basis only can one elucidate the mechanism of the reaction. This type of study was done in the preceding chapters. Here we are describing the method used to calculate various protonated and unprotonated species of ligands at different pH. The law of mass action provides the necessary basis for such calculations giving the relevant stability constants. The equilibrium between metal ions and molecules or ions with which it complexes can be expressed in terms of formation constants. In any given system the major complexes that are formed and their concentrations will be determined by the stability constants of all possible complexes (including metal chelates), the pH of solution, and the pK_a values of complexing species. However, whenever more than one type of metal ion and several different ligands are present at the same time an iterative approach should be used. Such an approach although possible by conventional means is extremely laborious unless a digital computer is used. A computer

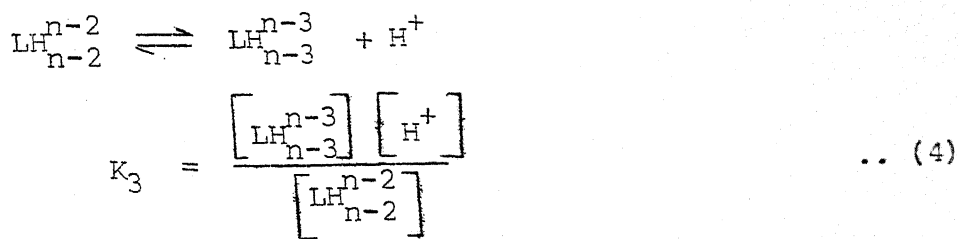
programme for an IBM 7044 was given by Perrin and Sayce¹ to calculate the equilibrium concentration of all species in multi-metal multi-ligand mixtures.

Calculation of Concentration of Protonated Forms of Ligands

The percentage content of the protonated forms of ligands may be calculated from the following equations deduced from the equations for the partial dissociation constants and the equations for the total concentration of the various dissociated forms:



$$\text{or } \beta_2 = \frac{[\text{LH}_{n-2}^{n-2}][\text{H}^+]^2}{[\text{LH}_n^n]} \quad \dots (3)$$



$$\beta_3 = \frac{[LH_{n-3}^{n-3}][H^+]^3}{[LH_n^n]} \quad \dots (5)$$

In general one can write

$$LH_n^n \rightleftharpoons LH_{n-m}^{n-m} + m H^+$$

$$\beta_m = \frac{[LH_{n-m}^{n-m}][H^+]^m}{[LH_n^n]} \quad \dots (6)$$

where n is the number of dissociable protons in the ligand and m can take value from 1 to n ; $K_1, K_2, K_3, \dots, K_m$ are the step-wise dissociation constants of the ligand while $\beta_1, \beta_2, \beta_3, \dots, \beta_m$ are the overall dissociation constants of the ligand.

$$C_{total} = [LH_n^n] + [LH_{n-1}^{n-1}] + [LH_{n-2}^{n-2}] + \dots + [LH_{n-m}^{n-m}] \quad \dots (7)$$

where,

C_{total} = concentration of total ligand.

The equilibrium concentration of any protonated ligand at a particular pH may be calculated from the following equation derived (by substitution) from Equations 1-7.

$$[LH_{n-m}^{n-m}] = \frac{C_{total} [H^+]^{n-m} K_1 K_2 K_3 \dots K_m}{[H^+]^n + K_1 [H^+]^{n-1} + K_1 K_2 [H^+]^{n-2} + \dots + K_1 K_2 K_3 \dots K_m [H^+]^{n-m}} \quad \dots (8)$$

$$= \frac{C_{total} [H^+]^{n-m} / \beta_m}{[H^+]^n + \beta_1 [H^+]^{n-1} + \beta_2 [H^+]^{n-2} + \dots + \beta_m [H^+]^{n-m}} \quad \dots (9)$$

By substitution of corresponding dissociation constants in Equation (9) one can calculate the corresponding protonated ligand concentration. Actually Equation (9) will give the protonated form concentration as a fraction of total concentration of ligand. The percentage can be calculated after multiplying it by 100.

The percentage of the individual protonated form is given in figures of different chapters.

Calculation of Concentration of Metal Complex at a given pH

This programme which begins by calculating the equilibrium concentration of metal ions and ligands for a system containing all the metal ions but only one complexing species. (This is done by first finding free ligand concentration using an incremental method to solve an equation containing this quantity as unknown). Each of the complexing species in turn is iterated in this way so that preliminary sets of values are obtained for free metal ion concentration. All the values are greater than for corresponding multi-metal multi-ligand systems. Similarly the initial estimates of free ligand concentration are all smaller than the final values. Subsequent operations are designed to give a progressive alternate lowering of these computed free metal ion concentration and raising of the computed ligand concentration until all equilibria are satisfied simultaneously for the multicomponent systems.

Consider that M^a , M^b , M^c , --- represent different kinds of metal ions and L^r , L^s , L^t , ---- are different kinds of ligands. Any complex that can be formed from them can be represented by $(M^a) (M^b) (M^c) \text{-----}$
 $(L^r)_\rho (L^s)_\sigma (L^t)_\tau \text{----} (OH)_\omega$ where $\alpha, \beta, \gamma \text{----} \rho, \sigma, \tau$ --- may be a positive integer or zero and ω can be a positive integer (for hydrolysed species), zero or negative (for protonated species). The concentration of any one of these complexes including protonated ligand species and hydrolysed metal ion is then given by

$$C_j = \beta_j M^a M^b M^c \text{----} L^r L^s L^t \text{---} (OH) \dots (10)$$

where β_j is overall formation constant so that the total concentration of metal i can be

$$[M^i]_T = [M^i] + \sum_{j=1}^{j=n} p_{ij} C_j \dots (11)$$

where p_{ij} is the number of metal ions M^i in species j . A similar set of equations can be written for ligand concentration also.

$$[L^i]_T = [L^i] + \sum_{j=1}^{j=n} p_{ij} C_j \dots (12)$$

The computer reads the cards and the relevant set of values $\alpha, \beta, \gamma, \text{---}, \omega$ for each species and corresponding equilibrium constants. It then calculates the free metal and free ligand concentration by following the iterative method.

Beginning with the crude approximation that complex formation is negligible (so that $[M^i] = [M^i]_T$ and $[L^x]$ can be calculated from $[L^x]_T$ by using appropriate pK_a values). The machine computes the quantity on the right hand side of Eqn.(11) for each kind of metal ion and similarly for each complexing species to give quantities that can be designated as $[M^i]_T^{cal}$ and $[L^x]_T^{cal}$ respectively. The initial estimates of $[M^i]$ and $[L^x]$ are then replaced by $[M^i] ([M^i]_T / [M^i]_T^{cal})^{1/2}$ and $[L^x] ([L^x]_T / [L^x]_T^{cal})^{1/2}$. With these new estimates the calculations are repeated to obtain better values of $[M^i]$ and $[L^x]$. The process is continued until all values of $[M^i]_T^{cal}$ and $[L^x]_T^{cal}$ differ from corresponding values of $[M^i]_T$ and $[L^x]_T$ by less than a specified quantity. (For the results given in these tables this was 0.001% of $[M^i]_T$ and of $[L^x]_T$.)

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VITAE

Born on July 1, 1954 at Bulandshahr (Uttar Pradesh), Krishan Kumar passed his High School in 1969. He passed his Intermediate Science in 1971 from the Government Inter College, Bulandshahr. He took his B.Sc. and M.Sc. degrees in 1973 and 1975 respectively from the Agra College, Agra affiliated to the Agra University. He joined the Ph.D. programme in the Department of Chemistry, Indian Institute of Technology, Kanpur in July 1975, under the supervision of Professor P.C. Nigam.

